


QUALITATIVE ANALYSIS TABLES,
AND THE
REACTIONS OF CERTAIN ORGANIC SUBSTANCES.

LETTS.

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QUALITATIVE ANALYSIS TABLES,
AND THE
REACTIONS OF CERTAIN ORGANIC SUBSTANCES

BY

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P R E F A C E.

THIS little book has been written chiefly for my own students, but I shall be glad if it prove of service to others also.

The plan which I have always adopted in teaching qualitative analysis, has been to demonstrate in the class-room the reactions of the metals, acids, &c., embraced in the course, and to write on the board the explanatory reaction, and also in words the characteristic phenomena, in each case. Then when we came to the detection of unknown substances, I have also demonstrated the actual process and have written on the board the scheme—my students being instructed to carefully observe all that I do, to copy in their note books all that I write, and to repeat in the laboratory for themselves, what they have seen done in the class-room. In this way they gradually write their own text books *pari passu* with their work in the laboratory ; my object being to teach them to observe accurately, and at the same time to make them understand the scientific explanation of each process which they are performing.

I have always found this method of teaching satisfactory, and that a sound knowledge of the subject is both acquired and retained, infinitely better and more readily than if a text book is placed in the student's hands and he is told to make use of it.

The labour to the teacher by this method is, however, severe ; so I have decided to abate it somewhat by placing in the hands of my students a series of tables which shall embody the essence of the demonstrations they actually see. There are also other reasons for doing this, as experience has taught me that students never take down these tables accurately, and that there are many notes, &c., to the latter, which it is impossible to deal with on the board. Moreover, there is a lot of matter which medical students (and the book is largely, though by no means entirely, written for them) ought to have some knowledge of, which it is impossible to teach in a three months' course ; and although very anxious that they should pass their professional examinations, I have done my utmost to discourage the "cram" system.

So much by way of apology for adding yet another to the many similar books on the subject.

Every teacher has his own methods—acquired not only from his experience, but also largely through the researches of others—and this book embodies mine.

I have worked out all the different schemes repeatedly, and have had the very salutary comments of many hundreds of students who have gone through them.

Table VIII. is founded on what I believe to be the best quantitative method for separating the phosphate, and although somewhat tedious in carrying out it has always proved satisfactory.

Considerable trouble has been taken with Table IX., which as every chemist knows, embodies a very difficult and unsatisfactory subject, and the same remark applies to Table X. (Solubility Table), which has been re-written with the aid of Storer's Dictionary, Fresenius, and special experiments of my own. The subject though of great importance in qualitative analysis is often nearly ignored by both teachers and students, and although from the conflicting statements as to solubilities I feel sure that the table here given may be open to many criticisms, I trust that it may be an improvement on its predecessors.

The following are my authorities on certain special subjects treated of in this book,—Fresenius, Dittmar, Barfoed, Neubauer and Vogel, Otto, Roberts, Tollens, and Storer.

In conclusion, my best thanks are due to my assistant, MR. R. F. BLAKE, for the great care and attention he has exercised in correcting and revising the proof sheets.

E. A. LETTS.

QUEEN'S COLLEGE, BELFAST,
JUNE, 1892.

ANALYTICAL CLASSIFICATION OF THE METALS.

IN THIS BOOK THE METALS ARE ARRANGED AS FOLLOWS :—

GROUP I.—Metals precipitated by sulphuretted hydrogen from acidulated solutions of their salts.

Sub-Groups :—

1. Metals forming insoluble, or sparingly soluble chlorides—
Silver, Lead, Mercurous Mercury.
2. Metals whose sulphides are soluble in (yellow) sulphide of ammonium—
Tin, Antimony, Arsenic.
3. Metals not belonging to either of the first two sub-groups—
Copper, Bismuth, Cadmium, Mercuric Mercury, (Lead).

GROUP II.—Metals precipitated by sulphide of ammonium from solutions of their salts (or by sulphuretted hydrogen and an alkali).

GROUP III.—Metals not precipitated by sulphuretted hydrogen from solutions of their salts, under any conditions.

Sub-Groups :—

1. Metals precipitated by carbonate of ammonium (as carbonates), after adding chloride of ammonium and ammonia to solutions of their salts—
Barium, Strontium, Calcium.
2. **Magnesium**—not precipitated under the above conditions by carbonate of ammonium, but which gives a precipitate with a soluble phosphate.
3. Metals which give no precipitate with any of the above reagents—
Potassium, Sodium, (Ammonium).

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QUALITATIVE ANALYSIS TABLES

WITH NOTES AND EXPLANATIONS.

Examination of a Simple Substance for Acid and Base, or Metal and Nonmetal.

TABLE I.

THE SUBSTANCE IS IN SOLUTION.¹

1. Examine for the metal *first* by Table II., because the examination for the metal may give a clue to the acid present,² and also because the presence of certain metals may exclude a number of acids.³
2. Next examine for the acid by Table III. In examining for the acid it is often necessary to remove the metal present, or to replace it by an alkaline metal.⁴ To do this the solution is boiled with a slight excess of carbonate of soda, filtered, and the filtrate just neutralized with nitric acid.⁵

THE SUBSTANCE IS A SOLID.

1. Make a careful examination by dry way tests according to Table V., which in many cases will be sufficient to identify the compound. It is, however, advisable to examine the solid by wet way tests also.
2. To dissolve the substance separate portions are boiled (*A*) with water, and if necessary (*B*) with dilute and strong hydrochloric acid, (*C*) nitric acid, and (*D*) aqua regia (1 volume of strong HNO_3 and 3 volumes strong HCl).⁶
3. If the substance is soluble in water, its aqueous solution is at once examined for the metal by Table II., and for the acid by Table III.
4. If the substance is soluble in acids only, the acid solution is examined (after dilution)⁷ for the metal⁸ by Table II. To detect the acid⁹ (should its presence not have been indicated while dissolving the substance), the solid is boiled for some time with carbonate of soda,¹⁰ the solution filtered, just neutralized with nitric acid, and examined by Table III.
5. If the substance is insoluble in water and acids,¹¹ it is fused for some time with carbonate of soda on platinum foil. The fused mass is then boiled with water, filtered, and the acid (and in some cases the metal also) sought for in the filtrate after just neutralizing with nitric acid, while the metal is detected in the residue after dissolving it in hydrochloric or nitric acid.

NOTES TO TABLE I.

1. The reaction of the solution should be tried with litmus paper, for if it is neutral the presence of all those salts is excluded which are soluble in acids only (see Solubility Table, pp. 56, 57). Its colour ought also to be noticed and recorded.
2. Thus many of the volatile acids are detected on adding HCl, *e.g.*:—CO₂, N₂O₃, H₂S, SO₂, HCN, &c., while one or two are indicated on adding HCl and H₂S, *e.g.*, chromates (yellow or orange) give a green solution with precipitation of sulphur; manganates (green) and permanganates (violet) become colourless.
3. In fact all those acids which form insoluble compounds with the metal. Thus, supposing silver to be found, the acid could not be HCl, HBr, HI, &c. The student should consult the Solubility Table given on pp. 56, 57.
4. This is necessary in those cases where the metal interferes with the ordinary reactions of the acids. If the metal found belongs to the first group it is sometimes advisable to remove it by H₂S when the filtered solution contains the free acid. Thus, cyanide of mercury is a compound with which nearly all the ordinary tests for hydrocyanic acid fail, and boiling its solution with carbonate of soda does not precipitate the mercury, whereas H₂S readily decomposes it and leaves hydrocyanic acid in solution. If the metal belongs to the second group it is sometimes advisable to remove it by ammonia and sulphide of ammonium. Sulphuric acid may be employed to separate lead, barium, strontium and calcium from their salts. Speaking generally it is advisable to remove the metal before testing for the acid unless the former is one of the alkalis or ammonia.
5. The solution now contains nitrate of soda and the sodium salt of the acid, and can be examined in the ordinary way for acids, as the presence of nitric acid does not interfere with their reactions. The original substance or the carbonate of soda solution must of course be separately examined for nitric acid.
6. In dissolving the substance in acids any characteristic phenomena should be observed and noted, *e.g.*, evolution of the more volatile acids (see test (1), Table III.) ; separation of silica from alkaline silicates ; separation of sulphur (when dissolving in nitric acid or aqua regia) indicating a sulphide ; evolution of red fumes (when dissolving in nitric acid) indicating oxidation, etc.
7. It is often advisable to get rid of the bulk of the acid which has been used in dissolving the substance, before testing for the metal. This may be done best by evaporating the solution to a small bulk, also by partly neutralizing with carbonate of soda.
8. If the solid is soluble in hydrochloric acid it cannot contain Ag or Hg₂, the solution is therefore at once treated with H₂S.
9. The solid should also be examined for the less volatile acids by test (2), Table III. Hydrochloric acid interferes with the reactions of so many acids that it is scarcely advisable to test the solution (supposing the solid to have been dissolved in that acid) systematically for acids. The following may however be searched for in it—H₂SO₄, H₃BO₃, H₃PO₄, H₃AsO₄, H₂C₂O₄ and SiO₂. The same remark applies to aqua regia, but not to the same extent when nitric acid is the solvent.
10. In many cases it is better to fuse with carbonate of soda on platinum foil, boil with water, filter, neutralize the filtrate, and proceed as described.
11. The following compounds are the most important insoluble bodies :—*White*—PbSO₄, SrSO₄, BaSO₄, AgCl, AgCN, SnO₂, Sb₂O₃, CaF₂, SiO₂, and many silicates. *Yellow*—AgBr, AgI and S.

TABLE II.

Examination for a Single Metal in a Solution.

PRELIMINARY TESTS.

1. Notice the colour of the solution which in some cases affords an indication of the metal present.¹
2. Test for ammonia in a portion of the solution by warming it with caustic potash or soda.² If present, confirm by adding PtCl_4 to original solution—yellow crystalline precipitate indicates—**AMMONIA**.
3. Dip a piece of clean platinum wire in the solution and heat in the flame of a Bunsen burner. Repeat the experiment two or three times.

COMPOUNDS OF :—		COLOUR THE FLAME
Strontium	...	Crimson.
Calcium	...	Orange-red.
Barium	...	Yellowish-green.
Copper	...	Bluish-green.
Sodium	...	Yellow.
Potassium	...	Violet (crimson when seen through blue glass).
Lead, Antimony, and Arsenic	...	Livid blue (somewhat similar to the potassium flame).

SYSTEMATIC EXAMINATION.

- (1.) Add HCl drop by drop. If a precipitate forms, add a little more of the acid to see whether it is soluble in excess.³ Notice any characteristic phenomena (*c. g.*, effervescence, odour, &c.) which may occur on adding the acid.⁴ If a permanent white precipitate forms,⁵ examine it by the Table below. If no precipitate forms, pass on to (2.)

Table for the Examination of the Precipitate produced by Hydrochloric Acid (Sub-gr. 1 of Gr. 1).			
The HCl . Precipitate is :—	Decant the liquid and shake ppt. with NH_3 . It is :—	The Metal is :—	Confirmatory Tests in the Original Solution.
White, and curdles when shaken	Dissolved	SILVER	(1) K_2CrO_4 —crimson ppt. (2) KHO —brown ppt.
White, and crystalline	Unchanged	LEAD	(1) K_2CrO_4 —yellow ppt. (2) KI —yellow ppt. (3) H_2SO_4 —white ppt.
White or yellowish	Blackened	MERCURY (mercurous)	(1) K_2CrO_4 —brick-red ppt. (2) KHO —black ppt. (3) Reinsch's test

NOTES TO TABLE II.

1. Solutions of **Copper** salts have a blue or green colour.

	Nickel	"	an emerald-green colour.	Solutions of Chromates	have a yellow or orange colour.
"	"	"	"	" Manganates	" a green colour.
"	Cobalt	"	a pink colour.	" Permanganates	" a violet colour.
"	Chromium	"	a violet-green or green colour.	" Ferrocyanides	" a pale yellow colour.
"	Ferric	"	a yellow or brown colour.	" Ferricyanides	" a yellow to red colour
2. It is advisable to test for ammonia at this early stage as it may save the trouble of going through the whole scheme, and also because the action of caustic potash or soda on many metallic solutions is characteristic, and thus even in the absence of ammonia valuable information may be obtained.

THE PRECIPITATE PRODUCED BY CAUSTIC POTASH OR SODA IS:—			INDICATING THE PRESENCE OF:—		REMARKS.
Black	Mercurous Mercury	Very characteristic
Brown	Silver	"
Light blue—black when boiled	Copper	"
Yellow	Mercuric Mercury	"
Rust coloured	Ferric Iron	"
Dirty green—becoming brown on exposure to the air	Ferrous Iron	"
Apple-green	Nickel	"
Blue—dirty pink when boiled	Cobalt	"
White—becoming brown when shaken with air	Manganese	"
Green—soluble in excess—reprecipitated on boiling	Chromium	"
White	<div> <div>Soluble in excess</div> <div>Insoluble in excess</div> </div>	Lead, Antimony, Tin, Zinc, and Aluminum	"
		Cadmium, Bismuth, and sometimes Barium, Calcium, Strontium, and Magnesium.	"

3. Tartar emetic gives a white precipitate (SbOCl)—soluble in excess (forming SbCl_3). Avoid a large excess of HCl which may precipitate barium salts.
4. On adding HCl all the more volatile acids are driven out of their salts, and in many cases may be recognized by their odour or other characteristic properties, *e.g.*, CO_2 , N_2O_3 , SO_2 , HCN , H_2S , &c. Hyposulphites give at first no precipitate with HCl , but after a short time a yellow precipitate of sulphur appears and the solution smells of SO_2 .
5. This may also possibly be sulphur from decomposition of a hyposulphite. A coloured precipitate is formed when HCl is added to sulphides of arsenic, tin, and antimony, dissolved in sulphide of ammonium or other alkaline sulphide, and H_2S is given off at the same time. The colour of the precipitate is yellow in the case of arsenic and tin, and orange in that of antimony.

TABLE 11.—*Continued.*

(2.) If HCl fails to produce a precipitate or if the precipitate first formed redissolves in excess, add H_2S to the HCl solution, and if no immediate precipitate is produced, add much H_2S and boil for some time.⁶ If a precipitate forms, examine it by the subjoined Table. If no precipitate forms, or only one which is white,⁷ pass on to (3).

Table for the Examination of the Precipitate produced by Sulphuretted Hydrogen (Sub-grs. 2 and 3 of Gr. 1).

Pour off the solution (if possible) from the H_2S precipitate, and warm the latter with yellow sulphide of ammonium.⁸ If it dissolves, examine it by **A.** If it does not dissolve, by **B.**

A. (Sub-gr. 2 of Gr. 1.)		
The colour of the H_2S precipitate is here of importance. If brown, the metal must be Stannous Tin . If orange, Antimony . If yellow, Arsenic or Stannic Tin . To distinguish between the latter, boil another portion of the H_2S precipitate (from which, if possible, the solution has been decanted) with carbonate of ammonium. If the precipitate dissolves, the metal is Arsenic . If it does not dissolve, the metal is Stannic Tin .		
The H_2S Precipitate is :—	The Metal is :—	Confirmatory Tests in the Original Solution.
Brown	STANNOUS TIN	(1) $HgCl_2$ —a white or grey precipitate.
Orange	ANTIMONY	(1) Water in excess—white ppt. (2) A drop placed on platinum foil, and both drop and foil touched with zinc gives a black stain. ⁹
Yellow { <i>Insoluble</i> in boiling carbonate of ammonium <i>Soluble</i> in boiling carbonate of ammonium	STANNIC TIN	(1) On adding zinc and <i>dilute</i> HCl, the zinc dissolves with effervescence, and a spongy mass of tin remains. This when boiled with <i>strong</i> HCl gives $SnCl_2$ which forms (a) a brown ppt. with H_2S , and (b) a white or grey precipitate with $HgCl_2$.
	ARSENIC	To ascertain in what form the arsenic is present, add H_2S <i>alone</i> to the original solution. <i>Immediate yellow precipitate</i> indicates chloride or other salt of arsenic. Confirm in original solution by Marsh's or Reinsch's test. <i>Yellow colour only</i> indicates arsenious anhydride or an arsenite. Confirm in original solution (1) by the yellow ppt. with ammonio-nitrate of silver, (2) by the green ppt. with ammonio-sulphate of copper. <i>No colour and no precipitate</i> in the cold, but a yellow precipitate which forms slowly on boiling with HCl and much H_2S indicates arsenic acid or an arseniate. Confirm in original solution (1) by the yellow precipitate on boiling with excess of ammonium molybdate, and (2) by the white precipitate with NH_4Cl , NH_3 and $MgSO_4$.

NOTES TO TABLE II.—*Continued.*

6. Arsenic acid and sometimes stannic salts require long boiling with much H_2S and HCl before a precipitate is formed.
7. A white precipitate of sulphur indicates the presence of an oxidising agent or of SO_2 . Ferric chloride (yellow or brown solution) gives a precipitate of sulphur, and the solution becomes colourless (because a ferrous salt is produced). Chromates and bichromates (yellow or orange solution) also give a precipitate of sulphur and become green (because chromium chloride is produced). Manganates (green solution) and permanganates (violet solution) also become colourless (because manganous chloride is formed).
8. *Yellow* sulphide of ammonium which contains $(NH_4)_2S_3$ alone dissolves SnS_2 converting it in doing so into $SnS_{2.7}$. As_2S_3 , Sb_2S_3 and SnS_2 all combine with $(NH_4)_2S$ forming soluble thio-salts, *e.g.*, $As_2S_3 + (NH_4)_2S = 2(NH_4)AsS_2$ (sulpharsenite of ammonium).
9. Tartar emetic does not answer to these confirmatory tests unless previously mixed with HCl until the precipitate first formed has just redissolved in excess.

TABLE 11.—Continued.

B. (Sub-gr. 3 of Gr. 1.)		
If the H_2S precipitate is yellow, the metal must be CADMIUM . (Confirmatory tests in original solution, (1) KHO —white precipitate insoluble in excess, (2) NH_3 —white precipitate soluble in excess). If dark coloured, add KHO to the original solution.		
The Precipitate produced by KHO is:—	The Metal is:—	Confirmatory Tests in the Original Solution.
White { Insoluble in excess	BISMUTH	(1) K_2CrO_4 (excess)—yellow ppt. (2) SnCl_2 and KHO (excess)—a black ppt.
Blue—becoming black on boiling	LEAD ¹⁰	(1) K_2CrO_4 —yellow ppt. (2) KI —yellow ppt. (3) H_2SO_4 —white ppt.
Yellow	COPPER	(1) $\text{K}_4\text{Fe}(\text{CN})_6$ —mahogany coloured ppt. (2) NH_3 (excess)—dark blue solution.
	MERCURY (mercuric)	(1) KI —scarlet ppt. soluble in excess. (2) NH_3 —white precipitate.

(3.) If H_2S and HCl fail to produce a precipitate take a new portion of the original solution, mix it with about its own volume of NH_4Cl solution,¹¹ then add NH_3 until the mixture after shaking smells of it, and whether a precipitate forms or not, add $(\text{NH}_4)_2\text{S}$. If a precipitate forms, examine by the subjoined Table. If no precipitate forms, pass on to (4).

Table for the Examination of the Ammonium Sulphide Precipitate (Gr. 2).			
The $(\text{NH}_4)_2\text{S}$ Precipitate is:—	The Metal is:—	Add KHO to the Original Solution. The Precipitate formed is:—	Confirmatory Tests in the Original Solution.
Black <div> <div>Soluble in HCl</div> <div>Insoluble in HCl</div> </div>	IRON { FERROUS (FERRIC	Dirty green—becoming brown on exposure to air ... Rust coloured ...	(1) $\text{K}_3\text{Fe}(\text{CN})_6$ —dark blue ppt. (1) $\text{K}_4\text{Fe}(\text{CN})_6$ —dark blue ppt. (2) KCNS —blood-red colour
	{ NICKEL	Apple-green ...	(1) $\text{K}_4\text{Fe}(\text{CN})_6$ —greenish-white ppt. (2) $\text{K}_3\text{Fe}(\text{CN})_6$ —dirty green ppt. (3) NH_3 in excess —violet blue solution.
	{ COBALT	Blue—pink on boiling ...	(1) $\text{K}_4\text{Fe}(\text{CN})_6$ —green ppt. (2) $\text{K}_3\text{Fe}(\text{CN})_6$ —chocolate-brown ppt. (3) Blow pipe test with $(\text{NH}_4)_2\text{S}$ ppt. (borax bead).
	{ ZINC (ALUMINUM	White—soluble in excess. This solution and H_2S —white ppt. White—soluble in excess. This solution and H_2S —no ppt. White—insoluble in excess.	(1) $\text{K}_4\text{Fe}(\text{CN})_6$ —white gelatinous ppt. (2) NH_3 —white gelatinous ppt. easily soluble in excess. (1) Add KHO in excess, then NH_4Cl —white ppt. (2) NH_3 —white gelatinous ppt. scarcely soluble in excess.
White	PHOSPHATE OF LIME, Etc. ¹²	Green—soluble in excess to green solution, reprecipitated on boiling	(1) Blow pipe test with $(\text{NH}_4)_2\text{S}$ ppt. (borax bead).
White	CHROMIUM	White—brown on exposure to air	(1) Bleaching powder solution—black ppt. (2) Blow pipe test with $(\text{NH}_4)_2\text{S}$ ppt. (carbonate of soda bead).
Dirty green	MANGANESE		
Salmon coloured			

NOTES TO TABLE II.—*Continued.*

10. Dilute solutions of lead are not precipitated by HCl, hence lead may appear as a metal of Sub-gr. 3 of Gr. 1. On adding caustic potash in excess to such solutions the precipitate first formed ($\text{Pb}(\text{OH})_2$) dissolves so rapidly that its formation may not be noticed at all.
11. The object of adding chloride of ammonium is to prevent the precipitation of magnesium, should it be present, by the ammonia added subsequently.
12. A white precipitate produced by ammonia and not changed by $(\text{NH}_4)_2\text{S}$ may be due, (1) to a phosphate, borate, fluoride, silicate, or oxalate, of barium, strontium, calcium, or magnesium; or (2) silica from an alkaline silicate. In the case of (1), the original solution is strongly acid (or if a solid, it is only soluble in acids), also the precipitate produced by caustic potash is insoluble in excess, while in the case of (2) the original solution is strongly alkaline, and caustic potash produces no precipitate. If a phosphate, etc., is indicated, test separate portions of the original solution (or solid) for :—phosphoric acid, by the ammonium molybdate test; boracic acid, by the turmeric reaction; oxalic acid, by the KMnO_4 and sulphuric acid reaction; while a fluoride is detected by heating the precipitate produced by ammonia (or the original solid) with sulphuric acid (see test (2), Table III.). If a phosphate is present, dissolve the ammonia precipitate (or original solid) in the least possible quantity of HCl, add a considerable quantity of sodium acetate, next a few drops of acetic acid, and then ferric chloride until a little of the solution filtered from the precipitate (basic phosphate of iron) is distinctly red. Finally, add ammonia, and boil. Filter, and examine the filtrate for Ba, Ca, Sr, and Mg by tests (4) and (5). If a fluoride or borate is present, fuse the ammonia precipitate (or original solid) with carbonate of soda. Boil with water, filter, and dissolve residue in HCl. Neutralize with ammonia, and test for the metal by (4) and (5). If an oxalate is present, heat the ammonia precipitate (or original substance) to dull redness to convert it into a carbonate. Dissolve in HCl, neutralize with ammonia, and test for the metal by (4) and (5). If a silicate is present, evaporate the original solution to dryness with HCl, which renders the silica insoluble while the metal passes into solution.

T A B L E 11.—*Continued.*

(4.) If $(\text{NH}_4)_2\text{S}$ has failed to produce a precipitate take a new portion of the original solution, mix it as before with about its own volume of NH_4Cl solution, then add NH_3 until the mixture smells of it, lastly carbonate of ammonium, and boil. If a precipitate forms, examine by the subjoined Table. If no precipitate forms, pass on to (5).

Table for the Examination of a Metal of Sub-gr. 1 of Gr. 3.		
Add CaSO_4 to the Original Solution.		
Calcium Sulphate causes :—	The Metal is :—	Confirmatory Tests in the Original Solution.
An <i>immediate</i> white precipitate A white precipitate on <i>boiling</i> only No precipitate, even on boiling	BARIUM STRONTIUM CALCIUM	(1) K_2CrO_4 —yellow ppt. (2) The flame test (yellowish-green). (1) The flame test (crimson). (1) The flame test (orange-red). (2) $(\text{NH}_4)_2\text{C}_2\text{O}_4$ —white ppt.

(5.) If carbonate of ammonium fails to produce a precipitate, test for traces of calcium by adding a few drops of $(\text{NH}_4)_2\text{C}_2\text{O}_4^{13}$ (white precipitate, if calcium is present), and if no result, add Na_2HPO_4 to the same solution—white precipitate indicates—**MAGNESIUM**. (Confirmatory tests in original solution (1) NH_3 —white precipitate in the cold, (2) $(\text{NH}_4)_2\text{CO}_3$ —white precipitate on boiling).

(6.) If no result has been obtained up to the present time the metal must be potassium or sodium, both of which should have been indicated by the preliminary tests. Confirm **POTASSIUM** in the original solution by adding PtCl_4 (and if necessary some alcohol) which gives a yellow crystalline precipitate. Confirm **SODIUM** in the original solution by adding freshly prepared $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ (pyro-antimoniate of potassium) which gives a white crystalline precipitate.

NOTES TO TABLE II.—*Continued.*

13. Traces of calcium often escape detection altogether unless oxalate of ammonium is added as described.

TABLE III.

Examination of a Solution containing a Single Acid. (see p. 2.)

(Separate portions are employed for each of the tests).

(1.) Treat the solution with about one-third its volume of strong hydrochloric acid.* Shake, and if no characteristic odour or effect, boil:—

RESULT.	SHOWS PRESENCE OF:—	CONFIRMATORY TESTS IN THE ORIGINAL SOLUTION.
Effervescence in the <i>cold</i> with evolution of a colourless gas having no characteristic odour, but causing a turbidity in a drop of lime-water suspended on a glass rod, (or when the gas is poured on to lime-water contained in a tube, and afterwards shaken with it).	CARBONATE	(1) BaCl_2 or CaCl_2 —a white precipitate soluble in acetic acid with effervescence.
Effervescence in the <i>cold</i> with evolution of ruddy fumes having a characteristic odour.	NITRITE	(1) In a very dilute solution. Starch + KI + acetic acid—blue colour. (2) $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ —colour bleached. (3) $\text{Hg}_2(\text{NO}_3)_2$ —grey precipitate.
Evolution of a gas smelling of rotten eggs and causing paper moistened with acetate of lead to turn black. (A white or yellow precipitate of sulphur often appears on the addition of an acid to a sulphide, especially if the latter has been long prepared.)	SULPHIDE	(1) Nitro-prusside of sodium—violet coloration. (2) $\text{SbCl}_3 + \text{HCl}$ —orange precipitate. (3) $\text{AsCl}_3 + \text{HCl}$ —yellow precipitate.
Odour of burning sulphur.	SULPHITE	(1) AgNO_3 —white precipitate, blackened on warming. (2) Zinc + <i>dilute</i> H_2SO_4 —evolution of H_2S (detected as above) and white precipitate of sulphur. (3) Iodine solution—colour bleached. (4) $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ —colour bleached.
Solution remains clear for a short time then becomes turbid from separation of sulphur, and at the same time smells of burning sulphur.	HYPOSULPHITE (Thiosulphate)	(1) AgNO_3 in excess—precipitate first white, then becoming yellow, orange, brown, and finally black. (2) Iodine solution—colour bleached.

* Dilute sulphuric acid (1 vol. strong acid to 3 vols. of water) may be substituted with advantage.

White crystalline precipitate, and the odour of benzoic acid on warming.	BENZOATE	See page 16.
White gelatinous precipitate.	SILICATE	See page 16.
Characteristic odour of hydrocyanic acid (also often escape of CO_2 , as commercial alkaline cyanides contain large quantities of carbonates).	CYANIDE	(1) $\text{FeSO}_4 + \text{Fe}_2\text{Cl}_6 + \text{HCl}$ —a blue precipitate ("Prussian Blue") or blue to green coloration. (2) Boiled with yellow sulphide of ammonium until the mixture is colourless, then acidulated with HCl , gives a blood-red colour with Fe_2Cl_6 .
Evolution of chlorine (greenish-yellow gas of pungent and characteristic odour) which bleaches moist litmus paper. (The original solution also smells of the gas, and possesses bleaching properties.)	HYPOCHLORITE	(1) MnCl_2 —brown precipitate.
On boiling, the mixture gradually emits the odour of hydrocyanic acid, and the solution (previously yellow to red) becomes blue or bluish-green.	FERROCYANIDE	(1) Fe_2Cl_6 —deep blue precipitate. (2) CuSO_4 —mahogany coloured precipitate. (3) ZnSO_4 —white gelatinous precipitate. (4) AgNO_3 —white precipitate.
	FERRICYANIDE	(1) FeSO_4 —deep blue precipitate. (2) CuSO_4 —yellowish-green precipitate. (3) AgNO_3 —orange precipitate.
Solution, at first colourless, becomes yellow on boiling, and evolves a yellowish gas* smelling somewhat like chlorine ("euchlorine") bleaching litmus, etc.	CHLORATE	(1) Chlorates give no precipitate with AgNO_3 , but if their solutions are mixed with zinc and <i>dilute</i> sulphuric acid, they are slowly changed to chlorides, which then give a white precipitate with AgNO_3 .
(2.) One volume of the solution is mixed with from three to four volumes of concentrated sulphuric acid, and the mixture boiled †:—		
Evolution of pungent acid fumes which give a white precipitate with a drop of nitrate of silver suspended from a glass rod.	CHLORIDE	(1) AgNO_3 —a white precipitate which curdles when shaken, dissolves readily in ammonia, but is insoluble in nitric acid. (2) Warmed with MnO_2 and sulphuric acid, chlorine is evolved as a greenish-yellow gas of characteristic odour, which bleaches moist litmus paper.

* If dilute sulphuric acid is employed instead of hydrochloric acid no effect may be produced.

† If dilute sulphuric acid is employed in the preceding test a chlorate may escape detection, but will be here indicated by the production of peroxide of chlorine—a yellow gas which is violently explosive.

TABLE III.—Continued.

RESULT.	SHOWS PRESENCE OF:—	CONFIRMATORY TESTS IN THE ORIGINAL SOLUTION.
Evolution of pungent acid fumes, etc., and red vapours of peculiar odour.	BROMIDE	(1) AgNO_3 —a yellowish precipitate which curdles when shaken, dissolves <i>with some difficulty</i> in ammonia. Insoluble in nitric acid. (2) Chlorine-water—a yellow to brown colour. On shaking the mixture with chloroform, the latter becomes coloured brown.
Evolution of pungent acid fumes, etc., and violet vapours.	IODIDE	(1) AgNO_3 —a yellowish precipitate which curdles when shaken, is insoluble in ammonia (but is whitened by it). Insoluble in nitric acid. (2) Chlorine-water—a yellow to brown colour. (A) On shaking the mixture with chloroform, the latter becomes coloured violet. (B) On adding some of it to fresh starch solution, the latter becomes coloured blue. (3) HgCl_2 —a scarlet precipitate.
Evolution of pungent acid fumes which give no precipitate with silver nitrate, but the tube in which the mixture is heated assumes a peculiar greasy appearance, and the glass is etched.	FLUORIDE	(1) CaCl_2 —white gelatinous precipitate, soluble in HCl .
Smell of vinegar.	ACETATE	(1) Boiled with alcohol and sulphuric acid gives the characteristic odour of acetic ether. (2) Fe_2Cl_6 —a blood-red colour which (A) is bleached by HCl , (B) when diluted and boiled gives a rust coloured precipitate.
The mixture darkens <i>quickly</i> , and the escaping gases smell of burnt sugar.	TARTRATE	(1) AgNO_3 —white precipitate which becomes grey on warming. (If the white precipitate is dissolved in the smallest possible quantity of ammonia and the mixture warmed, metallic silver is deposited on the tube as a mirror.)
The mixture darkens <i>slowly</i> , and the escaping gases smell of burnt sugar.	CITRATE	(1) AgNO_3 —a white precipitate which does <i>not</i> become grey at once on warming.
Escape of CO which burns with a blue flame. (This test only succeeds with a solid oxalate or with a very strong solution.)	OXALATE	See below.

Escape of CO which burns with a blue flame.	FORMIATE	(1) AgNO_3 —a grey precipitate of metallic silver on heating. (2) HgCl_2 —a white or grey precipitate on heating. (3) Fe_2Cl_6 —reacts as with an acetate.
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(3.) Mix the solution with an equal volume of concentrated sulphuric acid, then add black oxide of manganese, and warm :—

Effervescence and escape of CO_2 , which gives a turbidity in a drop of lime water suspended from a glass rod, (or when the gas is poured on to lime water contained in a test-tube and afterwards shaken with it).	OXALATE	(1) CaCl_2 —white precipitate, soluble in HCl . (2) KMnO_4 and H_2SO_4 —the mixture is decolorized with effervescence.
Escape of chlorine (yellowish-green gas of characteristic odour which bleaches moist litmus paper).	CHLORIDE	See page 13.
Escape of bromine (brown vapours of characteristic odour).	BROMIDE	See above.
Escape of iodine (violet vapours).	IODIDE	See above.

(4.) Add chloride of barium.

White precipitate <i>insoluble</i> in hydrochloric acid.	SULPHATE	(1) $\text{Pb}(\text{NO}_3)_2$ —white precipitate sparingly soluble in nitric acid.
White precipitate <i>soluble</i> in hydrochloric acid.	SEVERAL ACIDS	
Yellow precipitate (and original solution yellow to orange).	CHROMATE	(1) $\text{Pb}(\text{NO}_3)_2$ —yellow precipitate. (2) $\text{Hg}_2(\text{NO}_3)_2$ —brick-red ppt. (3) AgNO_3 —dark red ppt. (4) Warmed with alcohol and H_2SO_4 , the solution becomes green and smells of aldehyde.

(5.) Add ferrous sulphate, then pour in concentrated sulphuric acid, the tube being held aslant.

Brown layer at the junction of the two fluids.	NITRATE	(1) Boil with metallic copper and concentrated sulphuric acid—brown vapours. (2) Mix with brucine and concentrated sulphuric acid—a transient rose colour, becoming yellow.
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TABLE III.—Continued.

(6.) Add excess of molybdate of ammonium, and warm.

RESULT.	SHOWS PRESENCE OF:—	CONFIRMATORY TESTS IN THE ORIGINAL SOLUTION.
Yellow precipitate	PHOSPHATE	(1) AgNO_3 —yellow precipitate. (2) NH_4Cl , NH_3 , and MgSO_4 —white crystalline precipitate.
	ARSENATE	(1) AgNO_3 —dirty red precipitate. (2) NH_4Cl , NH_3 , and MgSO_4 —white crystalline precipitate. (3) Boil with HCl and H_2S —yellow precipitate of As_2S_3 slowly precipitated.

(7.) Acidulate with hydrochloric acid, moisten a piece of turmeric paper with the solution, and dry.

The paper becomes pink and on moistening with an alkali, it becomes bluish-green.	BORATE	(1) On adding sulphuric acid and alcohol, and setting fire to the mixture in a porcelain dish, it burns with a flame tinged green at the edge.
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(8.) Add ferric chloride.

Blood-red colour <i>not bleached</i> by hydrochloric acid.	SULPHOCYANATE	(1) AgNO_3 —white precipitate, easily soluble in NH_3 , insoluble in dilute HNO_3 .
Blood-red colour <i>bleached</i> by hydrochloric acid.	ACETATE	See p. 14.
Dark blue precipitate.	FERROCYNIDE	See p. 13.
Buff coloured precipitate.	BENZOATE	(1) Heat with alcohol and sulphuric acid—characteristic odour of benzoic ether (see p. 13).

(9.) Evaporate to dryness with hydrochloric acid, and treat the residue with water.

A white powder or gelatinous residue remains.	SILICATE	(1) $(\text{NH}_4)_2\text{CO}_3$ —white gelatinous precipitate.
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TABLE IV.

Reactions of Acids.

(c.) Indicates that the reaction is characteristic.

	NITRATE OF SILVER.			CHLORIDE OF BARIUM.		CHARACTERISTIC REACTIONS IN THE ORIGINAL SOLUTION.
	Precipitate.	Ppt. + HNO_3 .	Ppt. + NH_3 .	Precipitate.	Ppt. + HCl .	
CARBONATE	Yellowish-white	Sol. (with effervescence)	Soluble	White	Sol. (with effervescence)	Effervescence with dilute acids. The escaping gas giving a turbidity with lime water.
CHLORIDE	White	Insoluble	Soluble (with ease)	None	—	Chlorine (yellowish-green bleaching gas) evolved when solution is warmed with $\text{MnO}_2 + \text{H}_2\text{SO}_4$.
BROMIDE	Yellowish	Insoluble	Sol. (with difficulty)	None	—	Bromine (brown vapours) evolved when solution is warmed with $\text{MnO}_2 + \text{H}_2\text{SO}_4$.
IODIDE	Yellowish	Insoluble	Insoluble (but whitened)	None	—	Iodine (violet vapours) evolved when solution is warmed with $\text{MnO}_2 + \text{H}_2\text{SO}_4$.
FLUORIDE	None	—	—	White	Soluble	Warmed with an excess of H_2SO_4 in a test tube, the glass assumes a greasy appearance and is etched.
NITRATE	None	—	—	None	—	Black ring with FeSO_4 and H_2SO_4 .
NITRITE	White	Soluble	Soluble	None	—	Effervescence with dilute acids. The escaping gas being red.
SULPHATE	Crystalline (forms only in a strong solution)	—	—	White	Insol. (c.)	The white precipitate with BaCl_2 insoluble in HCl .
SULPHITE	White (grey on boiling) (c.)	Soluble	Soluble	White	Soluble	Odour of SO_2 on adding acids.

TABLE IV.—Continued.

(c.) Indicates that the reaction is characteristic.

	NITRATE OF SILVER.			CHLORIDE OF BARIUM.		CHARACTERISTIC REACTIONS IN THE ORIGINAL SOLUTION.
	Precipitate.	Ppt. + HNO_3 .	Ppt. + NH_3 .	Precipitate.	Ppt. + HCl .	
	White* becoming yellow, orange, brown, and finally black (c)	Soluble	Soluble	White (forms only in strong solution)	Soluble	On adding HCl , the solution remains clear for a short time, then S separates and the solution smells of SO_2 .
SULPHIDE	Black	Insoluble (in dilute acid)	Insoluble	None	—	Odour of H_2S on adding acids, the escaping gas giving a black coloration with lead paper.
HYPPOCHLORITE	None†	—	—	None	—	Brown precipitate with a manganese salt.
CHLORATE	None	—	—	None	—	(1) After reduction with Zn and dilute H_2SO_4 , AgNO_3 gives a white precipitate. (2) HCl gives a yellow solution on warming, with odour of "euchlorine."
ACETATE	Crystalline (forms only in a strong solution)	Soluble	Soluble	None	—	Fe_2Cl_6 gives a blood-red colour which (\mathcal{A}) is bleached by HCl , (β) when diluted and boiled gives a red precipitate.
OXALATE	White	Sol. (with difficulty)	Soluble	White	Soluble	On adding H_2SO_4 and then KMnO_4 , the solution is decolorized with effervescence.
BORATE	Slightly yellow	Soluble	Soluble	White (unless very dilute)	Soluble	Turmeric paper moistened with the solution and HCl and dried gives a pink stain, turned blue by an alkali.

* Soluble in excess of an alkaline hyposulphite.

† Ordinary hypochlorites contain chlorides, which give a white precipitate with nitrate of silver.

PHOSPHATE	Yellow	Soluble	Soluble	White	Soluble	(1) Yellow precipitate with AgNO_3 . (2) Yellow precipitate on warming with excess of molybdate of ammonium.
ARSENATE	Dirty red (c.)	Soluble	Soluble	White*	Soluble	(1) Dirty red precipitate with AgNO_3 . (2) Yellow precipitate on warming with excess of molybdate of ammonium.
CYANIDE	White	Insoluble	Sol. (with difficulty)	None	—	On adding FeSO_4 , Fe_2Cl_6 and then HCl , the solution turns blue or green.
FERROCYANIDE	White	Insoluble	Insoluble	None	—	(1) CuSO_4 gives a mahogany coloured precipitate. (2) Fe_2Cl_6 gives "Prussian Blue."
FERRICYANIDE	Orange (c.)	Insoluble	Soluble	None	—	FeSO_4 —a dark blue precipitate.
TARTRATE	White (grey on boiling) (c.)	Soluble	Soluble	White	Soluble	Mixed with a few drops FeSO_4 , then <i>one</i> or <i>two</i> drops H_2O_2 , and finally, excess of KHO , gives a deep blue or violet colour.
CITRATE	White (unchanged on boiling)	Soluble	Soluble	White (unless solution is dilute)	Soluble	Excess of lime water no precipitate in the cold, but on boiling, white precipitate.
CHROMATE	Crimson (c.)	Soluble	Soluble	Yellow(c)	Soluble	When shaken with a drop or two of H_2SO_4 , some H_2O_2 and ether, the ether becomes blue.
SILICATE	Yellow	Soluble	Soluble	White	Soluble	The solution boiled with excess of HCl gives gelatinous silica.
BENZOATE	White	Decomposed with separation of Benzoic acid	Soluble	None	—	On warming with alcohol and H_2SO_4 , odour of benzoic ether.
SULPHOCYANATE	White	Insoluble	Sol. (with difficulty)	None	—	Blood red colour with Fe_2Cl_6 , not bleached by HCl .

* Forms slowly in dilute solution, formation hastened on warming.

TABLE V.

Detection of the more commonly occurring Acids and Bases or Metals and Nonmetals, by Dry Way Tests.

(1.) Heat some of the substance in a loop bent at the end of a piece of *clean* platinum wire, in the blow pipe flame. Repeat the experiment once or twice, moistening the substance on the platinum wire, each time before heating, with hydrochloric acid.

COMPOUNDS OF :—	COLOUR THE FLAME :—
STRONTIUM ...	Crimson.
CALCIUM ...	Orange-red.
BARIUM ...	Yellowish-green.
COPPER ...	Bluish-green.
SODIUM ...	Yellow.
POTASSIUM ...	Violet (crimson when seen through blue glass).
LEAD, ANTIMONY, and ARSENIC	Livid blue (somewhat similar to the potassium flame).
BORACIC ACID (Free) ...	Bright green.

(2.) A.—Prepare a “borax bead” by fusing some borax in a loop of clean platinum wire, pick up a small fragment of the substance on this bead and heat first in the outer, and then in the inner blow pipe flame.

COMPOUNDS OF :—	COLOUR THE BEAD IN :—	
	THE INNER FLAME	THE OUTER FLAME
COBALT ...	Blue.	Blue.
CHROMIUM ...	Emerald-green.	Emerald-green.
IRON ...	Bottle-green.	Yellow to brown.
NICKEL ...	Dusky grey.	{ Violet—hot.
MANGANESE	Colourless.	{ Yellow—cold.
COPPER ...	Red and opaque or colourless	Amethyst.
		{ Green—hot.
		{ Blue—cold.

B.—Prepare a carbonate of soda bead, in the same way as a borax bead. Heat some of the substance in it, in the outer flame.

COMPOUNDS OF :—		COLOUR THE BEAD :—
MANGANESE	...	Bluish-green.
SILICA	Colourless and transparent on cooling if enough silica is present, also effervescence during the fusion.

(3.) **A**—Heat some of the substance in a cavity scraped on charcoal, before the blowpipe.

NITRATES and CHLORATES	...	Deflagrate (<i>i.e.</i> , appear to burn with scintillations). (Usually) give odour of burning sulphur. Give white fumes, and emit the odour of garlic. Volatilize entirely. Give white masses which glow. These when moistened with nitrate of cobalt and again heated before the blowpipe become coloured. Zinc— <i>green</i> , aluminium— <i>blue</i> , magnesium— <i>faint pink</i> .
SULPHIDES	
Compounds of ARSENIC	
" " MERCURY, AMMONIUM, etc.	
" " ALUMINIUM, MAGNESIUM, and ZINC	

B—Heat some of the substance in a cavity scraped on charcoal, with plenty of carbonate of soda, before the blowpipe flame until no further action occurs. If any metallic beads separate, try their hardness and malleability in a mortar with the pestle. Notice whether an incrustation is formed on the charcoal in addition to the beads. If no beads are visible, elutriate some of the fused mass and search with a magnetized knife for iron, nickel, and cobalt (which adhere as grey powders). Examine the flux for sulphur (indicating a sulphide or sulphate originally present) by moistening with hydrochloric acid, and testing the escaping gases for sulphuretted hydrogen with lead paper.

COMPOUNDS OF :—		GIVE A BEAD WHICH IS :—	INCRUSTATION.
LEAD	White, soft (leaves a streak on paper).	Yellow to brown.
BISMUTH	...	"	"
ANTIMONY	...	" hard	White.
SILVER	"	None.
TIN	" soft	"
COPPER	...	Red, hard	"

TABLE VI.

Bunsen's Dry Way Tests.

These tests possess many advantages over the ordinary dry way reactions, not the least of which are, that they may be performed with very minute quantities of a substance, and that by their means a considerable number of bodies may be detected which cannot be recognized by the blowpipe.

In the tests a Bunsen burner is used of the form shown in Figure 1. It is provided with an air regulator **A**, and with a shade **B** (shown by the dotted lines in the figure) to steady the flame, the latter of which can be raised or lowered by screwing or unscrewing the collar **C**. The structure of the flame (when the air regulator is turned so that a luminous tip is formed about half way up the flame) is shown in Figure 2 representing it in section. It consists of three parts, (1) an inner cone consisting of the unburnt mixture of gas and air, (2) the luminous tip, and (3) the mantle surrounding the inner cone, which consists of the burning mixture of gas and air. Bunsen distinguishes six points in the flame, which are made use of in his tests. **A**, the *base of the flame*, which has a comparatively low temperature. **B**, a point situated at a height of rather more than one-third of the total length of the flame. This is the hottest point, and is called the *zone of fusion or point of highest temperature*. **C**, the *lower reducing zone* situated at the inner border of the zone of fusion. **D**, the *lower oxidising zone* situated at the outer border of the zone of fusion. **E**, the *luminous tip or upper reducing zone*, which is only produced on partly closing the air regulator. A piece of cold porcelain held in this part of the flame should not be blackened. The temperature here is high, and the burning gases (which contain no free oxygen) are rich in dense hydrocarbons or in free carbon, consequently this part of the flame possesses energetic reducing properties. **F**, the summit of the flame, which is also the *upper oxidising flame*. In using this point, the air regulator may be completely open.

COLOURED FLAMES.—The substance is heated in a loop of fine platinum wire (about as thick as a horse hair) at the base of the flame, when the most volatile compound vaporises first and imparts its characteristic colour to the flame, and this is often followed by the other substances in the order of their volatility, each imparting its characteristic colour.

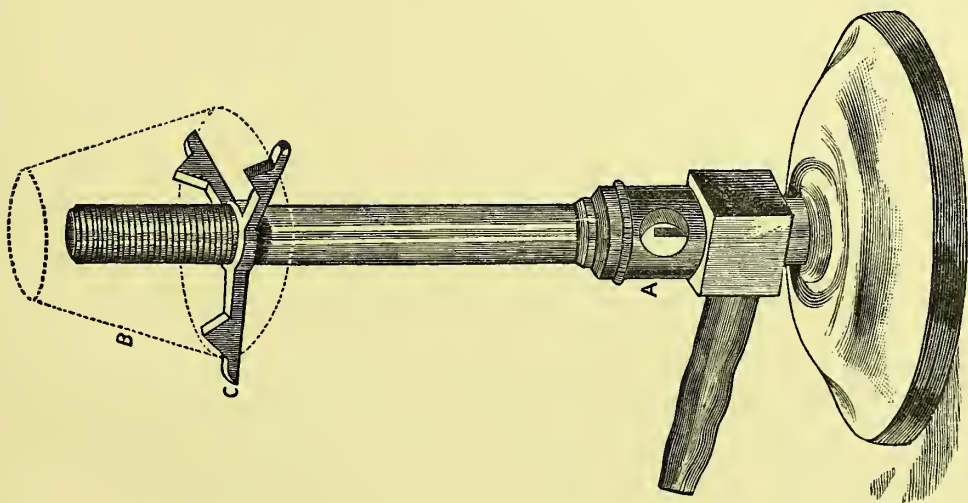


Fig. 1.

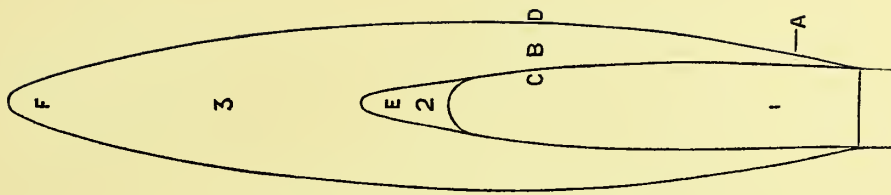


Fig. 2.

TABLE VI.—Continued.

FILMS.—A thread of asbestos about a quarter as thick as an ordinary match is moistened and applied to the finely powdered substance when some adheres. The substance thus supported is heated in the luminous tip of the flame, while a clean glazed porcelain basin containing some water is held immediately above it. If the substance contains a reducible and volatile element, the latter is liberated and collects as a film on the porcelain. Should an *oxide* film be required the substance is heated as before in the luminous tip, but the basin is held in the upper oxidising region, and the flame should be lowered to avoid scattering the oxide over too large a surface. Metallic films are recognized partly by their appearance and colour, partly by the action of dilute nitric acid (2 vols. of strong acid and 3 vols of water). Oxide films are recognized partly by their colour and partly by the action of certain reagents. *Iodide* films are obtained by exposing the oxide films to the fumes of hydriodic acid (obtained by allowing some iodine to act on a piece of moist phosphorus in a wide mouthed test tube). As soon as the iodide film has formed, it is examined by breathing upon it, when in certain cases it dissolves and vanishes, and also by blowing a stream of air upon it saturated with ammonia. Iodide films may be converted into *sulphide* films by blowing a current of air upon them saturated with sulphide of ammonium vapour. For this purpose a flask containing sulphide of ammonium is fitted with a cork through which two tubes pass, bent as for an ordinary wash bottle, with this difference that the tube through which the air is blown dips beneath the sulphide of ammonium, while the other, through which the air saturated with its vapour escapes, is short and just passes through the cork into the flask.

FILMS.			
	METALLIC.	OXIDE.	IODIDE.
MERCURY	Grey, which unites to globules	None formed, but metal deposited	Red or yellow*
SELENIUM	Cherry-red		Brown
ARSENIC	Black		Egg-yellow
ANTIMONY	"		Orange
BISMUTH	"		Bluish-brown
THALLIUM	"		Lemon-yellow
LEAD	"		Egg-yellow
CADMIUM	"		White
ZINC	"		White
TELLURIUM	"		Brown
			Black
			—
			Yellow
			Orange
			Brown
			—
			Black
			Lemon-yellow
			White
			—

* Obtained by exposing the metallic film to the vapour of iodine (which may be obtained by heating a fragment of iodine on the lid of a porcelain crucible).

ACTION OF REAGENTS ON THE FILMS.

	METALLIC FILM AND:— Dilute HNO ₃	OXIDE FILM AND :—			IODIDE FILM AND :—	
		SnCl ₂	SnCl ₂ +NaHO	NH ₃ + AgNO ₃ .	Moisture.	Ammonia.
MERCURY	Very slowly dissolved	—	—	—	Colour permanent	Vanishes, but reappears
SELENIUM	Scarcely attacked	Brick-red	Black	—	Vanishes partly	Permanent
ARSENIC	Scarcely attacked	—	—	Egg-yellow to brick-red	Vanishes, but slowly reappears	Colour permanently destroyed
ANTIMONY	Scarcely attacked	—	—	Black	Vanishes, but slowly reappears	Colour permanently destroyed
BISMUTH	Very slowly dissolved	White	Black	—	Vanishes to reappear	Becomes red or yellow, and brown when dry
THALLIUM	Very slowly dissolved	—	—	—	Colour permanent	Permanent
LEAD	Instantly dissolved	—	—	—	"	Vanishes, but reappears
CADMIUM	Instantly dissolved	—	—	—	"	—
ZINC	Instantly dissolved	—	—	—	—	—
TELLURIUM	Scarcely attacked	Black	Black	—	Vanishes, but reappears	Permanently destroyed

REDUCTION OF METALS.—For this purpose a crystal of washing soda is held near the flame until some of it has fused, and an ordinary wooden match is then thoroughly smeared with the fused salt. The match thus prepared is next cautiously heated until its end is completely carbonized, and thus a thin stick of charcoal is obtained saturated with carbonate of soda. The charred end of the match is next moistened with fused carbonate of soda, dipped into the finely powdered substance when some adheres, and heated in the lower reducing flame. The progress of the reduction is indicated by the effervescence of the globule of carbonate of soda. When it is complete the end of the stick is broken off and ground in an agate mortar with water. On pouring off the water and cautiously washing the residue, glittering spangles of the metal are left which may be dissolved in a suitable acid, and the solution tested by liquid reagents. To perform these liquid tests some of the solution may be allowed to rise in a fine capillary tube, and then the droplet expelled by blowing it on to a clean porcelain crucible lid. This may be tested with a droplet of the reagent taken up and expelled in a similar manner.

BORAX BEADS, etc., may also be obtained in the flame. For this purpose either a loop of very fine platinum wire is used to support the bead, or a straight and rather coarse wire with the bead adhering to its end. The beads may be heated either in the upper or lower reducing and oxidising flames.

A loop of wire may also be employed for obtaining the characteristically coloured masses which zinc, aluminum, and magnesium give when heated with nitrate of cobalt.

TABLE VII.

Examination of a Substance for Several Acids and Bases, or Metals and Nonmetals.

THE SUBSTANCE IS IN SOLUTION.

1. Examine for the metal *first* by Table VIII., because the examination for the metals often gives a clue to the acids present (see notes 7, 8, 9 and 10, pp. 35, 37), and also because the presence of certain metals may exclude a number of acids—in fact, all those acids which form insoluble compounds with them (see the Solubility Table pp. 56, 57).

2. Next examine for the acids by Table IX.

THE SUBSTANCE IS A SOLID.

1. Make a careful examination by dry way tests according to Table V., or better by Bunsen's tests described on Table VI.

2. Make a preliminary examination for acids according to Table IX., tests 1, 2 and 3.

3. To dissolve the substance for analysis¹ boil a little in a test tube with water, and, if necessary, with hydrochloric acid, dilute and strong; nitric acid, dilute and strong; and aqua regia; in succession,² pouring off the previous solvent in each case before trying the next. Whether any of the substance has been dissolved by each solvent, and roughly how much, may be ascertained by evaporating some of the extract to dryness on a slip of glass and noticing the amount of residue left.

A—The substance is entirely soluble in water. Examine its aqueous solution for the metals by Table VIII., and for the acids by Table IX.

B—The substance is not entirely soluble in water but is partly soluble in water and partly in acids. Examine the aqueous extract by itself for acids, and the acid extracts together for such acids as may possibly be present.³ As regards the examination for metals the aqueous and hydrochloric acid extracts may be mixed and examined together,⁴ while the same may be done sometimes, but not always, with the nitric acid and aqua regia extracts.⁵

NOTES TO TABLE VII.

1. If the substance is a metal or metallic alloy, heat at once with hydrochloric acid, and if it is not dissolved add nitric acid, evaporate to a small bulk, dilute slightly, filter if necessary from AgCl or PbCl₂. Dilute largely, and proceed according to Table VIII. In some cases it is better to dissolve in nitric acid alone. Preliminary experiments with a small quantity of the finely powdered substance will indicate the best solvent.

2. Notice any characteristic phenomena which occur on the addition of the acids.

In the treatment of a substance with hydrochloric acid there may be liberated as gases or vapours—

Carbonic anhydride	indicating carbonates.
Sulphurous anhydride	" sulphites or hyposulphites.
Sulphuretted hydrogen	" sulphides.
Hydrocyanic acid	" cyanides, ferrocyanides, or ferricyanides.
Chlorine	" chromates, peroxides and other strong oxidising agents.

Precipitates may be formed of:—

Sulphur (white or yellow)	from hyposulphites, polysulphides, thio-salts, etc.
Iodine (brown)	" iodides, along with oxidising agents.
Benzoic acid (white)	" benzoates.
Silica (white)	" silicates.
Chlorides (white)	" salts of silver, lead, mercurous mercury and barium.

The action of nitric acid or aqua regia may cause the formation of precipitates of sulphur (from sulphides, etc.) ; insoluble sulphates (from sulphides, etc., of barium, strontium and lead) ; chloride of silver (from silver or its compounds), etc. Hence the residue left on treatment of a substance with acids may contain a variety of things which were not originally present as such.

3. None of the more volatile acids are likely to be present, nor need they be tested for.

4. A precipitate produced on mixing the two extracts may be caused by the substances mentioned in note 8, p. 35, in addition to AgCl, PbCl₂ and Hg₂Cl₂.

5. The production of any precipitate on mixing a little of the two solutions, and if produced, an examination of its properties, will usually decide whether the two solutions should be mixed or not.

TABLE VII.—Continued.

C—The substance is insoluble⁶ in all the different solvents, or a portion of it is so. Heat a little of the insoluble portion on platinum foil to ascertain whether it contains sulphur or carbon. Fuse the remainder with carbonates of soda and potash and saltpetre.⁷ Boil with water, filter, and wash precipitate. The solution is examined for acids and metals, and the precipitate for metals, after dissolving in hydrochloric acid (or nitric acid if silver or lead is present).

NOTES TO TABLE VII.—Continued.

6. The following is a list of the principal insoluble bodies, together with the effect of fusing them with the mixed carbonates and saltpetre :—

* INSOLUBLE BODIES.	WHEN FUSED WITH THE MIXED ALKALINE CARBONATES AND SALTPETRE, GIVE: —
Sulphate of Lead ...	Carbonate of Lead insoluble in water, and sulphates of the alkalis which are soluble.
Sulphate of Barium ...	Barium " " "
Sulphate of Strontium ...	Strontium " " "
Haloids of Silver ...	" haloids " "
†Cyanide of Silver ...	" cyanides " "
Fluoride of Calcium ...	" fluorides " "
‡Silicates ...	Carbonate of Calcium " "
Oxide of Tin (native and ignited)	Carbonate or oxide of the metal, insoluble in water, and silicates of the alkalis which are soluble.
" Antimony (ignited) ...	Stannates of the alkalis which are soluble.
" Chromium " ...	Antimoniates " "
§Chrom Iron Ore ...	Chromates " "
Carbon ...	Oxide of Iron, insoluble in water, and chromates of the alkalis which are soluble.
Sulphur ...	Carbonic anhydride.
	Mostly volatilizes, but some may form sulphates of the alkalis which are soluble.

* Should be reduced to an impalpable powder before the fusion process.

† Cyanide of silver is decomposed when boiled with aqua regia, and gives chloride of silver.

‡ Silicates are best disintegrated by fusion in a platinum crucible with a mixture of 13 parts carbonate of potash, and 10 parts carbonate of soda.

To detect alkalis in them, heat in a platinum dish on a water bath, with about 4 parts fluoride of ammonium—and enough concentrated sulphuric acid to moisten the mixture—as long as visible vapours come off. Then heat until all the hydrofluoric acid and the excess of sulphuric acid are driven off. The residue is free from silica (which volatilizes as SiF₄) and contains the bases as sulphates, which as a rule are soluble in hydrochloric acid.

§ Chrome iron ore is best disintegrated by fusion with a mixture of 2 parts fused borax, and 3 parts of the mixed carbonates of potash and soda.

7. One part of the substance mixed with two parts carbonate of soda, two parts carbonate of potash, and one part nitrate of potash. In the absence of easily reducible metals (presence of which should have been detected in the preliminary examination) the fusion may be effected in a platinum crucible, or on a piece of platinum foil. If they are present the mixture must be fused in a porcelain crucible, which however has the drawback of introducing small quantities of silica and alumina. They may however be removed previous to fusion—lead sulphate by digesting with acetate of ammonia, haloids of silver, and cyanide of silver, by treatment with a strong solution of cyanide of potassium.

TABLE VIII.
Examination of a Solution for Several Metals.

PRELIMINARY TESTS.

1. Notice the colour of the solution.¹
2. Test the reaction of the solution with litmus paper. If it is acid, see whether it is strongly so by noticing the effervescence it gives with carbonate of soda, and roughly the amount of the latter required to neutralize it.²
3. Test for **AMMONIA** in a portion of the solution by warming it with caustic potash.³
4. Dip a piece of clean platinum wire in the solution, and heat in the flame of a Bunsen's burner. Repeat the experiment several times, and notice any flame coloration which may be produced.⁴

NOTES TO TABLE VIII.

1. Solutions of **Copper** salts have a blue or green colour.
 " **Nickel** " " an emerald green colour.
 " **Cobalt** " " a pink colour.
 " **Chromium** " " a violet green or pure green colour.
 " **Ferric** " " a yellow or brown colour.
 Of course in mixtures of the above the characteristic colours may be more or less masked.
2. Strongly acid solutions may contain several compounds which are insoluble in water, and are precipitated unchanged on neutralizing. As a consequence a number of substances may be found in the sulphide of ammonium precipitate which do not belong to Group 2. (see note 25.)
3. It is advisable to test for ammonia at this early stage, and also the action of caustic soda or potash on many metallic solutions is characteristic, and thus even in the absence of ammonia valuable information may often be obtained.

THE PRECIPITATE PRODUCED BY CAUSTIC SODA OR POTASH IS :—			INDICATING THE PRESENCE OF :—		REMARKS.
Black	Mercurous Mercury	Very characteristic
Brown	Silver	"
Light blue—black when boiled	Copper	"
Yellow	Mercuric Mercury	"
Rust coloured	Ferric Iron	"
Dirty green—becoming brown on exposure to air	Ferrous Iron	"
Apple-green	Nickel	"
Blue—dirty pink when boiled	Cobalt	"
White—becoming brown when shaken with air	Manganese	"
Green—soluble in excess—reprecipitated on boiling	Chromium	"
White	{ <i>Soluble</i> in excess <i>Insoluble</i> "	Lead, Antimony, Tin, Aluminum, and Zinc	"
		Cadmium, Bismuth, and sometimes Barium, Strontium, Calcium, and Magnesium	"
			
			

4.

COMPOUNDS OF :—		COLOUR THE FLAME :—	
Strontium	...	Crimson	
Calcium	..	Orange-red	
Barium	...	Yellowish-green	
Copper	...	Bluish-green	
Sodium	...	Yellow	
Potassium	...	Violet (crimson when seen through blue glass)	
Lead, Antimony, and Arsenic	..	Livid blue (somewhat similar to the potassium flame)	
Boric Acid (free)	..	Bright green	

TABLE VIII.—Continued.

SYSTEMATIC EXAMINATION.⁵

- (1.) Add hydrochloric acid drop by drop. If a precipitate forms, add a little more of the acid to see whether it is soluble in excess.⁶ Notice any characteristic phenomena (e.g., effervescence or odour) on adding the acid.⁷ If a permanent white precipitate forms,⁸ filter it off, and examine by the Table given below. If no precipitate forms (or one soluble in excess), pass on to (2).

Table for the Examination of the Precipitate produced by Hydrochloric Acid (Sub-gr. 1 of Gr. 1).		
Wash the precipitate once or twice with cold water, rejecting the washings. Then rinse the precipitate into a test-tube or beaker, boil with water, and filter :—		
Residue (may contain AgCl and Hg ₂ Cl ₂).	Solution (may contain PbCl ₂).	
Transfer by means of a spatula to a test tube, shake with strong ammonia, and filter :—	Add to separate portions of the solution :— (1) K ₂ CrO ₄ —yellow ppt. (2) H ₂ SO ₄ —white ppt. (3) KI—yellow ppt. soluble in hot water. Indicate— LEAD.	
Residue (black)=NH ₂ Hg ₂ Cl. Dissolve by heating with a little strong HCl and a granule of KClO ₃ , and boil until the chlorine is expelled. To separate portions of the solution add :— (1) KI—scarlet ppt. (2) KHO—yellow ppt. Indicate—	Solution (may contain 2AgCl, NH ₃). Boil to expel most of the ammonia (white precipitate=AgCl), and add HNO ₃ . White precipitate indicates— SILVER.	
	MERCURY (mercurous).	

NOTES TO TABLE VIII.—*Continued.*

5. If the number of metals present in the solution is known, it is better before examining the different group precipitates, to see how many of the latter there are, because it may happen that each group precipitate has only to be examined for one metal. Thus supposing a solution is given for the detection say of three metals, and the latter are silver, aluminum, and magnesium. If the student runs through the scheme he finds that he has three different group precipitates, viz. :—one produced by HCl, one by $(\text{NH}_4)_2\text{S}$, and one by Na_2HPO_4 , and consequently he knows that each precipitate can contain but one metal. On the other hand if he first examines the HCl precipitate for several metals and then the $(\text{NH}_4)_2\text{S}$ precipitate in a similar manner he obviously wastes much time and energy.
6. Tartar emetic gives a white precipitate (SbOCl)—soluble in excess (forming SbCl_3). Avoid a large excess of HCl which may precipitate barium salts, and prevent the precipitation of certain metals of Group 1, especially cadmium.
7. On adding HCl all the more volatile acids are driven out of their salts, and in many cases may be recognised by their odour or other characteristic properties, *e.g.*, CO_2 (escaping with effervescence), N_2O_3 (escaping with effervescence and production of red fumes) SO_2 , HCN , H_2S , etc. Hyposulphites give at first no precipitate with HCl, but after a short time a yellow precipitate of sulphur appears and the solution smells of SO_2 .
8. This may also possibly be sulphur from decomposition of a hyposulphite. A coloured precipitate is formed when HCl is added to sulphides of arsenic, tin, and antimony, dissolved in sulphide of ammonium or other alkaline sulphide, and H_2S is given off at the same time. The colour of the precipitate in the case of arsenic and tin is yellow, and orange in that of antimony.

TABLE VIII.—*Continued.*

- (2.) Some of the solution filtered from the HCl precipitate, or in which that reagent has failed to produce a precipitate, is mixed in a test tube with much H_2S water, and if no immediate precipitate appears, the mixture is boiled for some time.⁹ If no precipitate forms, or one which is white only,¹⁰ pass on to (3). If a precipitate forms, the whole of the solution is treated with H_2S (gas) until the precipitate settles easily, leaving a clear solution above. The mixture is filtered, and the filtrate tested with more H_2S gas (to be certain that the whole of the metals have been precipitated).

Table for the Examination of the Precipitate produced by Sulphuretted Hydrogen (Sub-grs. 2 and 3 of Gr. 1).

Wash the precipitate two or three times with water (rejecting the washings); then transfer some of it to a test tube, boil with *yellow* sulphide of ammonium and filter. Add excess of HCl to the filtrate. If the precipitate is pure white, or at most slightly yellow, examine the whole of the H_2S precipitate by **B**, but if decidedly yellow or orange, boil the whole of the H_2S precipitate with *yellow* sulphide of ammonium.¹¹ Filter, and examine the residue by **B**, the solution by **A**.

A (may contain As_2S_3 , Sb_2S_3 and SnS_2 as thio-salts) (Sub-gr. 2 of Gr. 1).		
Reprecipitate the sulphides by adding HCl in excess, ¹² filter, and wash two or three times with water. Transfer the precipitate to a beaker, and boil with a solution of carbonate of ammonium (saturated in the cold). ¹³		
Residue (may contain SnS_2 and Sb_2S_3).	Solution (may contain As_2S_3 and As_2O_3).	
Wash, transfer by a spatula to a test tube, and boil for some time with strong HCl, which dissolves both sulphides (any residue is sulphur and traces of As_2S_3). Dilute the solution.	<p>Acidify with HCl, and if necessary add H_2S—a yellow precipitate indicates—</p> <p style="text-align: center;">ARSENIC.</p> <p>Confirm by boiling the precipitate with strong nitric acid to obtain arsenic acid. Filter, and test portions of filtrate with :—</p> <p>(1) Excess of molybdate of ammonium, and heat—yellow ppt. (2) NH_4Cl, NH_3 in excess, and $MgSO_4$—white ppt.</p>	
<p>1. Test a few drops of the solution by placing them on a piece of zinc on platinum foil. A black stain on the platinum indicates—</p> <p style="text-align: center;">ANTIMONY.</p> <p>(The presence of antimony in the solution may be confirmed by Marsh's test, and <i>sometimes</i> by the white precipitate formed on adding much water to the solution).</p>	<p>2. To the rest of the solution add a few fragments of <i>pure</i> zinc (best electrolyzed zinc which dissolves rapidly). Wait until all effervescence has ceased. If a spongy metallic mass remains, pour off the liquid, and boil the latter with strong HCl until effervescence ceases.¹⁴ Dilute (filter if necessary), and test the solution by adding :—</p> <p>(1) H_2S—brown ppt. (2) $HgCl_2$—white or grey ppt.</p> <p>Indicate—</p> <p style="text-align: center;">TIN.</p>	

NOTES TO TABLE VIII.—Continued.

9. Arsenic acid and sometimes stannic salts require long boiling with much H_2S and HCl before a precipitate is formed.
10. A white precipitate of sulphur indicates the presence of an oxidizing agent or of SO_2 . Ferric chloride (yellow or brown solution) gives a precipitate of sulphur and the solution becomes colourless (because a ferrous salt is produced). Chromates and bichromates (yellow or orange solution) also give a precipitate of sulphur and become green (because chromium chloride is produced). Manganates (green solution) and permanganates (violet solution) also become colourless (because manganous chloride is formed).
11. *Yellow* sulphide of ammonium which contains $(NH_4)_2S_2$ alone dissolves SnS , converting it into SnS_2 . As_2S_3 , Sb_2S_3 , and SnS_2 all combine with $(NH_4)_2S$ forming thio-salts, *e.g.*, $As_2S_3 + (NH_4)_2S = 2NH_4AsS_2$ (sulpharsenite of ammonium).
12. On adding hydrochloric acid the soluble thio-salts of tin, antimony, and arsenic are decomposed, the sulphides of those metals being precipitated. Thus $2NH_4AsS_2 + 2HCl = 2NH_4Cl + As_2S_3 + H_2S$. Yellow sulphide of ammonium is decomposed by hydrochloric acid with precipitation of sulphur which is *white*. Thus $(NH_4)_2S_2 + 2HCl = 2NH_4Cl + S + H_2S$.
13. This acts on As_2S_3 forming a mixture of arsenite and sulpharsenite of ammonium. Thus $4As_2S_3 + 4(NH_4)_2CO_3 = 2(NH_4)AsO_2 + 6(NH_4)AsS_2 + 4CO_2$.
14. Zinc reduces stannic chloride to metallic tin. Thus $SnCl_4 + 2Zn = 2ZnCl_2 + Sn$; and strong hydrochloric acid dissolves the tin to stannous chloride. Thus $Sn + 2HCl = SnCl_2 + H_2$.

TABLE VIII.—Continued.

B (may contain HgS, CuS, PbS, CdS and Bi ₂ S ₃) (Sub-gr. 3 of Gr. I).		
Wash two or three times with water, transfer the precipitate by a spatula to a beaker or test tube, and boil with <i>strong</i> HCl. ¹⁵ Dilute and filter :—		
Residue (may contain HgS and CuS).	Solution (may contain PbCl ₂ , CdCl ₂ , BiCl ₃ , and traces of CuCl ₂).	
Transfer by a spatula to a beaker or test tube, and boil with HCl and a granule of KClO ₃ until all has dissolved (except a little sulphur), and the smell of chlorine has entirely passed off. Dilute, filter if necessary (blue solution indicates copper). Test portions with :—	Evaporate in a porcelain basin cautiously until the solution is nearly dry (<i>i.e.</i> , until only a drop or two remains). Add a few drops of dilute HCl, taking care that any of the solidified residue is thoroughly wetted. <i>Pour</i> off the solution :—	
(1) KI—scarlet ppt. indicates—	Solution (may contain BiCl ₃ , CdCl ₂ , and traces of CuCl ₂).	
MERCURY (mercuric).	1.	2.
(2) NH ₃ (excess)—dark blue solution (white ppt. further proves Hg) indicates—	Test a few drops of the solution by adding SnCl ₂ and KHO in large excess. Black precipitate indicates— BISMUTH.	Dilute the solution largely, and filter from any BiOCl which separates as a white powder. Pass H ₂ S, and if the ppt. is not yellow (yellow ppt.=CdS) collect it on a filter, boil with a mixture of one part concentrated H ₂ SO ₄ and three parts water (to dissolve CdS). ¹⁶ Filter, and dilute largely with H ₂ S solution. Yellow precipitate indicates—
COPPER.	LEAD.	CADMIUM.

NOTES TO TABLE VIII.—*Continued.*

15. Dilute nitric acid may be substituted for strong hydrochloric acid, in which case all the metals are dissolved except mercury. The filtered solution may be mixed with hydrochloric acid and evaporated nearly to dryness, etc., as described, and the copper detected in a portion of the solution poured off from the lead chloride, either by ferrocyanide of potassium (mahogany coloured precipitate or solution), or by excess of ammonia (blue solution).
16. Another method of separating copper from cadmium consists in treating the mixed sulphides with a strong solution of cyanide of potassium which dissolves the sulphide of copper, leaving the yellow sulphide of cadmium undissolved.

TABLE VIII.—Continued.

- (3.) Some of the solution filtered from the H_2S precipitate, or in which that reagent has failed to produce a precipitate, is mixed with its own volume of chloride of ammonium,¹⁷ ammonia in slight excess (*i.e.*, until after shaking, the solution smells of it), and whether a precipitate forms or not, sulphide of ammonium is added. If no precipitate forms, pass on to (4); but if a precipitate forms, the whole solution is treated with NH_4Cl , NH_3 and $(\text{NH}_4)_2\text{S}$ —avoiding large excess of the latter's—boiled and filtered. The filtrate is tested with a little more $(\text{NH}_4)_2\text{S}$ to be certain that the whole of the metals have been precipitated. The $(\text{NH}_4)_2\text{S}$ precipitate may consist (1) simply of the metals of Group 2, and (2) in addition to these, of Ba, Ca, Sr, and Mg, in combination with certain acids viz :— H_3PO_4 , SiO_3 , H_2BO_3 , $\text{H}_2\text{C}_2\text{O}_4$ and HF . As the treatment of the precipitate varies in the two cases, it must first be examined for the acids mentioned¹⁸ unless it is known that they are absent.

Table for the Examination of the Sulphide of Ammonium Precipitate, ²⁰ when Phosphates, &c., are absent (Gr. 2).		
Transfer the ppt. (after washing two or three times with hot water) to a beaker or test tube, and stir well with dilute HCl (1 part strong acid to 5 parts water). Filter :—		
Black Residue (may contain NiS and CoS).	<p>Test for COBALT by the borax bead. If it is absent, the residue must be NiS. The NICKEL may be identified both by the borax bead, and also by dissolving the residue in hot HCl and a granule of KClO_3, boiling to get rid of excess of acid, and then adding excess of K_2CO_3 to obtain the characteristic apple-green precipitate.</p> <p>If Co is present, the residue is tested for Ni as follows :—It is first dissolved in hot HCl and a granule of KClO_3 (filtering off any sulphur if necessary)—the solution nearly neutralized with KHO, and KCN added until the ppt. first formed redissolves in excess. The fluid is then shaken with bromine (added drop by drop) until it is yellow and smells of bromine. Excess of KHO is next added, when a black ppt. indicates—</p> <p style="text-align: right;">NICKEL.²⁴</p>	<p>Solution (may contain Zn and Mn as ammonia double salts).</p> <p>Pass H_2S through the solution until saturated, a ppt. indicates—</p> <p style="text-align: right;">ZINC.²³</p> <p>Filter. Add $(\text{NH}_4)_2\text{S}$, a ppt. indicates—</p> <p style="text-align: right;">MANGANESE.</p>
Precipitate (may contain $\text{Al}_2(\text{OH})_6$, $\text{Fe}_2(\text{OH})_6$, $\text{Cr}_2(\text{OH})_6$, $\text{Mn}(\text{OH})_2$).	<p>Wash once or twice with boiling water, and fuse in a nickel dish with pure NaHO (or KHO) and a little KClO_3,²² and heat until the fused mass is red hot. Allow to cool. A green mass indicates—</p> <p style="text-align: right;">MANGANESE.</p> <p>Boil with water (and add a few drops of alcohol if much Mn is present). Filter. Slightly acidulate filtrate with nitric acid, then add slight excess of NH_3, and boil. A gelatinous ppt. indicates—</p> <p style="text-align: right;">ALUMINUM.</p> <p>Filter (yellow solution indicates Cr). Acidulate with acetic acid, and add a solution of lead chloride. A yellow ppt. indicates—</p> <p style="text-align: right;">CHROMIUM.</p>	

17. The object of adding chloride of ammonium is to prevent the precipitation of magnesium, should it be present, by the ammonia added subsequently.
18. In case the solution contains nickel, its sulphide dissolves to some extent in yellow sulphide of ammonium, and on filtering, the filtrate is brown—which is very characteristic of nickel. If this happens, the filtrate must be boiled for some time to get rid of the excess of sulphide of ammonium and again filtered from the NiS which separates.
19. It is easier to test for H_3PO_4 &c., in the solution filtered from the H_2S precipitate instead of in the $(NH_4)_2S$ precipitate itself. Separate portions of the solution (freed from H_2S by boiling) are examined as follows :—
 - A.—By boiling with excess of molybdate of ammonium—yellow precipitate indicates—*phosphoric acid*.
 - B.—By adding H_2SO_4 and then $KMnO_4$ —effervescence due to the escape of CO_2 and the solution decolorized indicates—*oxalic acid*.
 - C.—By evaporating to dryness, moistening with strong HCl, and water—insoluble gelatinous residue indicates—*silicic acid*.
 - D.—" " on turmeric paper—pink stain, turned blue on addition of alkalis, indicates—*boracic acid*.
 - E.—" " and heating the residue in a test tube with strong H_2SO_4 , when the glass assumes a peculiar greasy appearance and is etched indicating—*hydrofluoric acid*.
- Phosphate of calcium may be extracted as such from the $(NH_4)_2S$ precipitate by digesting the latter with acetic acid. The filtered solution then gives a white precipitate with $(NH_4)_2C_2O_4$ proving the presence of calcium, and a yellow precipitate when boiled with an excess of molybdate of ammonium proving the presence of phosphoric acid.
20. If the $(NH_4)_2S$ precipitate is pure white it cannot contain Fe, Ni, Co, or considerable quantities of Cr. On the other hand a dark coloured precipitate may contain all the metals of Group 2.
21. This method of separation is based on the fact that $Fe_3(OH)_6$, $Cr_3(OH)_6$, and $Al_3(OH)_6$ are insoluble in excess of ammonia ($Cr_3(OH)_6$ and $Al_3(OH)_6$ are slightly soluble, but are reprecipitated on boiling off the excess)—while $Zn(OH)_2$ and $Mn(OH)_2$ are soluble, the former entirely, the latter partly—especially in the presence of ammonia salts.
22. On fusing with KHO and $KClO_3$, the chromium is converted into K_2CrO_4 , the manganese into $KMnO_4$, the aluminium into $Al_4(OK)_6$ —all three of which are soluble in water, while the iron is converted into Fe_3O_3 which is insoluble. Alcohol destroys the $KMnO_4$ so that the aqueous solution of the fused mass eventually contains $Al_4(OK)_6$ (which is decomposed by HNO_3 and NH_3 giving $Al_3(OH)_6$), and K_2CrO_4 which gives yellow chromate of lead with a solution of lead chloride.
23. The precipitate consists of ZnS which is often dark coloured from traces of NiS and CoS. The zinc may be confirmed in the precipitate by the film test (p. 26) or by redissolving it in dilute HCl, adding slight excess of ammonia, boiling until the solution is faintly acid and reprecipitating with H_2S when the precipitated ZnS is usually pure white.
24. This method of separation depends upon the following facts. Both Co and Ni are precipitated by cyanide of potassium as cyanides soluble in excess, forming respectively cobalto-cyanide of potassium— $4KCN, Co(CN) = K_4Co(CN)_6$ and double cyanide of nickel and potassium— $2KCN, Ni(CN)_2 = K_2Ni(CN)_4$. On adding bromine the *cobalto*-cyanide is converted into *cobalti*-cyanide. Thus $2K_4Co(CN)_6 + Br_2 = 2K_3Co(CN)_6 + 2KBr$. On now adding caustic potash the double cyanide of nickel and potassium is decomposed with formation (in presence of the hypobromite) of black $Ni_3(OH)_6$, while the cobalti-cyanide remains unchanged. The cobalt may be separated from the solution filtered from the black $Ni_3(OH)_6$, by neutralizing with HNO_3 and adding mercurous nitrate when a white precipitate is produced (mercurous cobalti-cyanide) which on ignition leaves black Co_3O_4 .
- Another method of separation consists in adding to the solution containing cobalt and nickel a lump of nitrite of potassium, and a sufficiency of acetic acid, and allowing the mixture to stand in a warm place for 12 hours. The whole of the cobalt is then precipitated as a yellow compound $K_3Co(NO_2)_6$. The nickel may be separated from the solution filtered from this precipitate by KHO, and the resulting precipitate tested by the borax bead.

TABLE VIII.—Continued.

Table for the Examination of the Sulphide of Ammonium precipitate ²⁰ when Phosphates, &c., are present. ²⁵		
Transfer the precipitate (after washing two or three times with water) to a beaker or test tube, and stir well with dilute HCl (1 part strong acid to three parts water), filter :—		
Black Residue (may contain NiS & CoS).	Solution (may contain FeCl ₂ , Cr ₂ Cl ₆ , Al ₂ Cl ₆ , ZnCl ₂ , MnCl ₂ ; H ₃ PO ₄ , H ₂ BO ₃ , H ₂ C ₂ O ₄ , HF, SiO ₂ ; and CaCl ₂ , SrCl ₂ , BaCl ₂ , MgCl ₂).	
Test for COBALT by the borax bead. If it is absent, the residue must be NiS. The NICKEL may be identified both by the borax bead, and also by dissolving the residue in hot HCl and a granule of KClO ₃ , boiling to get rid of excess of acid, and then adding excess of K ₂ CO ₃ to obtain the characteristic apple-green ppt. If Co is present, the residue is tested for Ni as follows :—It is first dissolved in hot HCl and a granule of KClO ₃ (filtering off any sulphur if necessary)—the solution nearly neutralized with KHO, and KCN added until the ppt. first formed redissolves in excess. The fluid is then shaken with bromine (added drop by drop) until it is yellow and smells of bromine. Excess of KHO is next added when a black ppt. indicates—		
NICKEL. ²⁴		
	Residue (may contain BaSO ₄ , CaSO ₄ , SrSO ₄ and SiO ₂). ²⁷	Solution (may contain Fe ₂ (SO ₄) ₃ , Cr ₂ (SO ₄) ₃ , Al ₂ (SO ₄) ₃ , ZnSO ₄ , MnSO ₄ ; H ₃ PO ₄ ; and possibly traces of H ₂ BO ₃).
		Test a little of the solution with K ₃ Fe(CN) ₆ , a blue ppt. indicates— IRON . If present, boil the solution with a few crystals of solid KClO ₃ until the smell of chlorine is apparent. Evaporate to dryness, and heat the residue with strong sulphuric acid until effervescence ceases and dense white fumes of H ₂ SO ₄ come off. ²⁶ Add about 20 c.c. of water to the residue, stir well, and then add an equal volume of alcohol. Allow to settle, and filter :—
	Precipitate (may contain Al ₂ (OH) ₆ , Fe ₂ (OH) ₆ , Cr ₂ (OH) ₆ , Mn(OH) ₂).	Solution (may contain Zn and possibly Mn as ammonia double salts, also MgSO ₄).
		Evaporate to about 5 c.c. If H ₃ PO ₄ is present proceed by A , if not, pass on to B . A —Add 50 c.c. of molybdate of ammonium.* Heat nearly to boiling, and maintain for about 15 minutes at that temperature. Filter, and warm the filtrate with a little more molybdate to be certain that all the H ₃ PO ₄ has been precipitated. ²⁸ Just neutralize with NH ₃ , boil for some time, and filter :— B —Dilute with water, just neutralize with NH ₃ , boil for some time, and filter :—
	Wash once or twice with boiling water and fuse in a nickel dish with pure NaHO (or KHO) and a little KClO ₃ , and heat until the fused mass is red hot. ²⁹ Allow to cool. A green mass indicates—	Precipitate
		Indicates— ZINC , (and possibly traces of Mn.)
	MANGANESE. Boil with water (and add a few drops of alcohol if much Mn is present). Filter. Slightly acidulate filtrate with nitric acid, then add slight excess of NH ₃ , and boil. A gelatinous ppt. indicates—	Solution
		Add Na ₂ HPO ₄ White ppt. indicates— MAGNESIUM.
	ALUMINUM. Filter (yellow solution indicates Cr). Acidulate with acetic acid, and add a solution of lead chloride, a yellow ppt. indicates—	
	CHROMIUM.	

* The ordinary solution, which contains molybdate of ammonium, nitrate of ammonium and excess of nitric acid.

NOTES TO TABLE VIII.—Continued.

25. The sulphide of ammonium precipitate may contain phosphates, borates, fluorides, silicates, and oxalates, not only of the metals of Group 2, but also of barium, calcium, strontium, and magnesium, because these compounds though insoluble in water are soluble in dilute acids, hence in such cases the original solution has a strong acid reaction. On neutralizing with ammonia they are reprecipitated unchanged and thus appear in the sulphide of ammonium precipitate.
26. By this treatment all the metals are completely converted into sulphates; oxalic acid is destroyed ($\text{H}_2\text{C}_2\text{O}_4 - \text{H}_2\text{O} = \text{CO} + \text{CO}_2$), hydrofluoric acid is expelled completely, and boracic acid partly at least. On adding water and alcohol the sulphates of barium, calcium, and strontium remain undissolved while the remaining metals and phosphoric acid pass into solution.
27. If this precipitate is entirely soluble in a large quantity of water, it consists of CaSO_4 only. If not, it is first tested for calcium by treating it with cold water, filtering, and adding oxalate of ammonium to the filtrate. The residue is boiled for ten minutes with a solution of one part carbonate and three parts sulphate of potassium, collected on a filter, washed, and then treated with dilute hydrochloric acid which will dissolve the resulting carbonates of calcium and strontium, and leave the sulphate of barium which remains unaltered. Strontium may be detected in the HCl solution by evaporating it to dryness, dissolving in water and testing with calcium sulphate.
28. By this treatment the phosphoric acid is entirely removed as a yellow powder consisting of phospho-molybdate of ammonium— $2(\text{NH}_4)_3\text{PO}_4, 22\text{MoO}_3, 12\text{H}_2\text{O}$ —if the precautions mentioned are strictly observed.
29. On fusing with KHO and KClO_3 , the chromium is converted into K_2CrO_4 , the manganese into KMnO_4 , the aluminum into $\text{Al}_2(\text{OK})_6$ —all three of which are soluble in water, while the iron is converted into Fe_2O_3 which is insoluble. Alcohol destroys the KMnO_4 so that the aqueous solution of the fused mass eventually contains $\text{Al}_2(\text{OK})_6$ (which is decomposed by HNO_3 and NH_3 giving $\text{Al}_2(\text{OH})_6$) and K_2CrO_4 which gives yellow chromate of lead with a solution of lead chloride.
30. Care must be taken to avoid excess of sulphide of ammonium or protracted heating, lest the molybdic acid present in the solution should become reduced to insoluble sulphide of molybdenum.

TABLE VIII.—Continued.

(4.) A little of the solution filtered from the sulphide of ammonium precipitate, or in which that reagent has failed to produce a precipitate, is first tested by boiling with carbonate of ammonium. If no ppt. forms, pass on to (5), but if a ppt. forms, the whole solution is mixed with carbonate of ammonium, boiled, and filtered. The filtrate is tested with a little more carbonate of ammonium to be certain that the whole of the metals have been precipitated. The ppt. is washed once or twice with water, rejecting the washings.

Table for the Examination of the Precipitate produced by Carbonate of Ammonium (Sub-gr. 1 of Gr. 3). ³¹		
Dissolve in acetic acid, using as little of the acid as possible. Add neutral chromate of potassium.		
Precipitate.	Solution (may contain $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$).	
Yellow. Indicates— BARium.	Test a portion with CaSO_4 . White ppt. on warming indicates— STRONTIUM . If no ppt. forms, test another portion for calcium with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (white ppt.). If Sr is present, add H_2SO_4 to the rest of the solution, allow to stand some time, and filter.	
Confirm by the flame test, also by the immediate white ppt. which CaSO_4 gives in the acetic solution of the $(\text{NH}_4)_2\text{CO}_3$ ppt.	Precipitate (may contain SrSO_4 and CaSO_4).	Solution (may contain CaSO_4).
	Wash twice or thrice with cold water, then test the subsequent washings with NH_3 and $(\text{NH}_4)_2\text{C}_2\text{O}_4$. White ppt. indicates—	Neutralize with NH_3 and add $(\text{NH}_4)_2\text{C}_2\text{O}_4$. White ppt. indicates—

CALCIUM.³²

- (5.) The solution filtered from the carbonate of ammonium precipitate, or in which that reagent has failed to produce a precipitate, is first tested with a few drops of oxalate of ammonium (which may precipitate traces of Ca),³³ filtered if necessary, and a little of it tested for magnesium with Na HPO_4 . White crystalline ppt. indicates—**MAGNESIUM**. If Mg is present, examine by (7). If absent, by (6).
- (6.) *In the absence of magnesium* the solution is tested for potassium and sodium as follows:—It is evaporated to dryness in a porcelain (or better—platinum) dish, and calcined until all ammonia salts are driven off. (It is safer to redissolve the residue, to filter from any slight residue which may be left, and once more to evaporate to dryness, and calcine). The residue is then tested with the flame test for potassium (violet flame, crimson through blue glass), and sodium (yellow flame). The rest is then dissolved in a little water, the **POTASSIUM** confirmed in a portion of the solution by PtCl_4 (yellow crystalline ppt.), and the **SODIUM** in another portion of the solution by freshly prepared pyroantimoniate of potassium (white crystalline ppt. on stirring).
- (7.) *If magnesium is present*, it should be removed before testing for K and Na. To do this, evaporate to dryness, and drive off the ammonium salts. Treat the residue with water, and boil with excess of hydrate of barium or milk of lime.³⁴ Filter, add excess of carbonate of ammonium, boil, filter, and proceed according to (6).

NOTES TO TABLE VIII.—*Continued.*

31. By examining a little of this precipitate by flame tests, the presence of barium or strontium, and sometimes of both together may often be ascertained.
32. Another method of separating calcium from strontium is as follows :—Precipitate their carbonates from the acetic acid solution (containing chromate of potassium) by boiling with ammonia and carbonate of ammonium—wash, dissolve in dilute nitric acid, and evaporate the solution to complete dryness. Then treat with alcohol to which a little ether may be added, which dissolves nitrate of calcium, but leaves the whole of the nitrate of strontium.
33. Small quantities of calcium salts are not precipitated by carbonate of ammonium in presence of large quantities of ammonium salts.
34. By this treatment the magnesium is converted into insoluble hydrate, but barium hydrate is introduced into the solution. It is, however, completely removed subsequently by treatment with carbonate of ammonium.

TABLE IX.

Examination of a Solution for Several Acids.

The examination of a solution for a considerable number of acids is often a long and tedious operation, and may go beyond the resources of analysis altogether, as the reactions of many acids interfere with each other more or less completely. The examination is greatly simplified if the number of acids present is known, and is comparatively easy when only two or three are present. The plan here proposed consists (1) of a preliminary examination (which in many cases will lead to the detection of all the acids present), and (2) of a scheme for the separation of certain acids from each other or for detecting them in each others presence. The examination for the metals should be made previous to the examination for the acids, and the Solubility Table consulted (pp. 56, 57), as the presence of certain metals excludes that of certain acids, and also because during the examination for metals certain of the acids may have been detected (see notes 7, 8, 9 and 10, pp. 35, 37).

In making the preliminary examination, tests (1), (2), (3), and (4) may be made with the *original* solution (except in very exceptional cases, such as cyanide of mercury and chloride of mercury—see note 4, p. 3), but for the remaining tests the solution must be freed from metals other than potassium, sodium, and ammonium, and as a rule the same remark applies to all the confirmatory tests. To obtain a solution free from the heavy metals different plans¹ may be adopted, according to the circumstances of the case. The most general one consists in boiling with excess of carbonate of soda, when the heavy metals are precipitated as carbonates or hydrates, while the acids become sodium salts. Some of the filtered solution is first tested for a nitrate by test (4), and the rest just neutralized with nitric acid, *i.e.*, nitric acid must be cautiously added until the effervescence ceases and a drop of the solution produces no marked change with either red or blue litmus paper.

PRELIMINARY EXAMINATION.²

(1.) Add dilute sulphuric acid (1 vol. strong acid to 3 vols. water), and if no immediate effect, warm the mixture.

RESULT.	SHOWS PRESENCE OF : —	CONFIRMATORY TESTS ³ IN NEUTRAL SOLUTION FREE FROM HEAVY METALS.
Effervescence in the <i>cold</i> , the escaping gas having no characteristic odour but causing a turbidity with lime water.	CARBONATE	
Effervescence in the <i>cold</i> , with evolution of ruddy fumes having a characteristic odour.	NITRITE	(1) Starch + KI + acetic acid—blue colour. (2) Mercurous nitrate gives a grey precipitate of metallic mercury.

NOTES TO TABLE IX.

1. Acids may be separated as such from the metals of Group 1 by the action of sulphuretted hydrogen ; from the metals of Group 2 by sulphide of ammonium ; and from lead, barium, calcium, and strontium, by means of sulphuric acid and alcohol.

2. In addition to this preliminary examination the following observations should also be made :—

A.—The colour of the original solution (chromates—yellow to orange ; ferricyanides—yellow to red ; ferrocyanides—pale yellow ; manganates—green ; permanganates—violet).

B.—The reaction of the original solution to test paper.

C.—The effect of heat on the residue left, when the original solution is evaporated to dryness—to detect organic acids. (This is done best by evaporating some of the solution to dryness on platinum foil, and heating the residue.)

3. These consist of the reactions specially characteristic of each acid, but it does not follow that they will always succeed : for instance, take the case of a nitrite in presence of a sulphide, sulphite, or hyposulphite. The confirmatory test for the nitrite with starch, iodide of potassium, and acetic acid, may not succeed because the other acids present will absorb the liberated iodine. In such cases the acids present which interfere with the reactions of the one suspected must be removed, and here the knowledge and ingenuity of the analyst come into play. In the above instance all of the three interfering acids can be removed by nitrate of silver : the filtered solution, however, contains excess of nitrate of silver which would interfere with the confirmatory test for the nitrite. To remove it, chloride of sodium in excess may be added, and the filtered solution will now give a blue colour with starch, iodide of potassium, and acetic acid. No general rules can be given for such cases.

TABLE IX.—Continued.

RESULT.	SHOWS PRESENCE OF :—	CONFIRMATORY TESTS IN NEUTRAL SOLUTION FREE FROM HEAVY METALS.
Evolution of a gas smelling of rotten eggs and causing paper moistened with acetate of lead to turn black. (A white or yellow precipitate of sulphur often appears on the addition of an acid to a sulphide, especially if the latter has been long prepared.)	SULPHIDE	(1) Nitro-prusside of sodium and caustic soda gives a reddish-violet coloration.
Odour of burning sulphur.	SULPHITE	(1) Zinc and dilute sulphuric acid cause evolution of H_2S (detected as above) and a white precipitate of sulphur.
The solution remains clear for a short time, then becomes turbid from separation of sulphur, and at the same time smells of burning sulphur.	HYOSULPHITE (Thiosulphate)	(1) Silver nitrate in excess gives a white precipitate at first, which becomes yellow, orange, brown, and finally black.
White crystalline precipitate, and the odour of benzoic acid on warming.	BENZOATE	See page 51.
White gelatinous precipitate.	SILICATE	See page 51.
Characteristic odour of hydrocyanic acid.	CYANIDE*	(1) $FeSO_4 + Fe_2Cl_6 + HCl$ —a blue precipitate ("Prussian Blue") or blue to green coloration. (2) Boiled with yellow sulphide of ammonium until the mixture is colourless, then acidulated with HCl , gives a blood-red colour with Fe_2Cl_6 .
Evolution of a greenish-yellow gas of pungent and characteristic odour which bleaches moist litmus paper. (The original solution also smells of the gas, and possesses bleaching properties.)	HYPOCHLORITE†	(1) $MnCl_2$ —brown precipitate.
On boiling, the mixture gradually emits the odour of hydrocyanic acid, and its colour (previously yellow to red) becomes blue or bluish-green.	FERROCYANIDE	(1) Fe_2Cl_6 —deep blue precipitate.
	FERRICYANIDE	(1) $FeSO_4$ —deep blue precipitate.

* If an alkaline cyanide is present the solution has the odour of hydrocyanic acid, even before adding the sulphuric acid. Cyanide of mercury does not respond to most of the tests for cyanides. To detect the hydrocyanic acid in it, the mercury may be precipitated by sulphuretted hydrogen, when the (filtered) solution will contain the free acid.

† If hypochlorites always contain chlorides.

(2.) Evaporate some of the solution to a small bulk (or better to dryness), and heat the residue in a test tube with excess of strong sulphuric acid.

Evolution of a yellow and very explosive gas having a chlorous odour (peroxide of chlorine).	CHLORATE	(1) Chlorates give no precipitate with silver nitrate, but if their solutions are mixed with zinc and dilute sulphuric acid they are slowly changed to chlorides which then give a white precipitate with silver nitrate.
Evolution of pungent acid fumes which give a white precipitate with a drop of silver nitrate suspended from a glass rod.	CHLORIDE	(1) Warmed with MnO_2 and H_2SO_4 , chlorine is evolved as a greenish-yellow gas of characteristic odour, which bleaches moist litmus paper. (2) $AgNO_3$ —a white precipitate which curdles when shaken, dissolves readily in ammonia, but is insoluble in nitric acid.
Evolution of pungent acid fumes, etc., and red vapours of peculiar odour.	BROMIDE	(1) Chlorine water—a yellow to brown colour. On shaking the mixture with chloroform, the latter becomes coloured brown.
Evolution of pungent acid fumes, etc., and violet vapours.	IODIDE	(1) Chlorine water (not in excess)—a yellow to brown colour. (A) On shaking the mixture with chloroform, the latter becomes coloured violet. (B) On adding some of it to fresh starch solution, the latter becomes coloured blue. (2) $HgCl_2$ —a scarlet precipitate.
Evolution of pungent acid fumes which give no precipitate with $AgNO_3$, but the tube in which the mixture is heated assumes a greasy appearance, and the glass is etched.	FLUORIDE	(1) $CaCl_2$ —white gelatinous precipitate, soluble in HCl .
Smell of Vinegar.	ACETATE	(1) The dry substance (or residue left when the solution is evaporated to dryness) heated with solid arsenious anhydride, gives the characteristic odour of kakodyl.
The mixture darkens <i>quickly</i> , and the escaping gases smell of burnt sugar.	TARTRATE	(1) Ferrous sulphate and <i>one</i> or <i>two</i> drops of peroxide of hydrogen, and lastly excess of caustic potash give a beautiful violet colour. (Distinction from citric acid and other organic acids.) (2) $AgNO_3$ —a white precipitate which becomes grey on warming. (If the precipitate is dissolved in the smallest possible quantity of ammonia, and the mixture warmed, metallic silver is deposited on the tube as a mirror.)
The mixture darkens <i>slowly</i> , and the escaping gases smell of burnt sugar.	CITRATE	(1) $AgNO_3$ —a white precipitate which does <i>not</i> at once become grey on boiling.

TABLE IX.—Continued.

RESULT.		SHOWS PRESENCE OF :—		CONFIRMATORY TESTS IN NEUTRAL SOLUTION FREE FROM HEAVY METALS.
Escape of CO which burns with a blue flame.		OXALATE		See below.
Escape of CO which burns with a blue flame.		FORMIATE		(1) AgNO_3 —a grey precipitate of metallic silver on heating. (2) HgCl_2 —a white or grey precipitate on heating.
(3.) Mix the solution with an equal volume of concentrated sulphuric acid, then add black oxide of manganese, and warm.				
Effervescence and escape of CO_2 which gives a turbidity in a drop of lime water suspended from a glass rod (or when the gas is poured on to lime water contained in a test tube and afterwards shaken with it).		OXALATE		(1) CaCl_2 —a white precipitate, soluble in HCl . (2) KMnO_4 and H_2SO_4 —the mixture is decolorized with effervescence.
Escape of chlorine (yellowish-green gas of characteristic odour which bleaches moist litmus paper).		CHLORIDE		See page 49.
Escape of bromine (brown vapours of characteristic odour.		BROMIDE		See page 49.
Escape of iodine (violet vapours).		IODIDE		See page 49.
(4.) Add ferrous sulphate, then pour in strong sulphuric acid, the tube being held aslant.				
Brown layer at the junction of the two fluids.		NITRATE*		(1) Boiled with metallic copper and strong sulphuric acid the <i>original solution</i> gives brown vapours of characteristic odour. (2) Mixed with brucine and strong sulphuric acid the <i>original solution</i> gives a transient rose colour quickly becoming yellow.
(5.) Test separate portions of the neutralised solution free from heavy metals as follows :— A.—Add chloride of barium.				
White precipitate <i>insoluble</i> in nitric acid.		SULPHATE†		(1) $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ —white precipitate, sparingly soluble in nitric acid.
White precipitate <i>soluble</i> in nitric acid.		SEVERAL ACIDS		
Yellow precipitate (and the original solution yellow to orange).		CHROMATE		(1) $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ —yellow precipitate. (2) $\text{Hg}_2(\text{NO}_3)_2$ —brick-red precipitate.

* An iodide interferes with this test, and should be removed before it is performed.

† This reaction though very characteristic and delicate may fail in the presence of certain salts, such as chloride of ammonium, nitrate of ammonium, etc., which have the power of dissolving sulphate of barium.

B.—Add excess of molybdate of ammonium, and heat.

Yellow precipitate.	PHOSPHATE	(1) AgNO_3 —yellow precipitate. (2) NH_4Cl , NH_3 , and MgSO_4 —white crystalline precipitate.*
	ARSENATE	(1) AgNO_3 —dirty red precipitate. (2) NH_4Cl , NH_3 , and MgSO_4 —white crystalline precipitate. (3) Boiled with HCl and much H_2S —yellow precipitate of sulphide of arsenic is slowly formed.

C.—Acidulate with hydrochloric acid, moisten a piece of turmeric paper with the solution, and dry.

The paper becomes pink, and on moistening with an alkali it turns bluish-green.	BORATE	(1) On adding H_2SO_4 and alcohol, and setting fire to the mixture in a porcelain dish, it burns with a flame tinged green at the edge.
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D.—Add ferric chloride.

Dark blue precipitate.	FERROCYANIDE	(1) CuSO_4 —mahogany coloured precipitate.
Blood red colour, <i>not bleached</i> by hydrochloric acid.	SULPHOCYANATE	(1) AgNO_3 —white precipitate, easily soluble in NH_3 , insoluble in dilute HNO_3 .
Blood-red colour, <i>bleached</i> by hydrochloric acid.	ACETATE	See page 49.
Buff-coloured precipitate.	BENZOATE	(1) Heat with alcohol and sulphuric acid—characteristic odour of benzoic ether.

E.—Evaporate to dryness with hydrochloric acid, treat the residue with strong hydrochloric acid, and then with water.

A white powder or gelatinous residue remains.	SILICATE	(1) $(\text{NH}_4)_2\text{CO}_3$ —white gelatinous precipitate.
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* An excellent confirmatory test for a phosphate, which will succeed in the presence of nearly all other acids, consists in heating the solid substance (or residue left on evaporating the solution to dryness) in a hard glass tube with magnesium wire before the blow-pipe, until the magnesium has melted and become incandescent. On throwing the contents of the tube into water, phosphuretted hydrogen is evolved (from the resulting phosphide of magnesium), and may be recognised even in minute quantities by its odour.

TABLE IX.—*Continued.*

The preceding preliminary examination will probably have indicated the following with certainty :—carbonate, nitrite, fluoride, sulphate, sulphide, hypochlorite, borate, chromate, silicate, benzoate, and one or more of the following groups, (1) chloride, bromide, or iodide ; (2) nitrate or nitrite ; (3) sulphite or hyposulphite ; (4) chlorate or hypochlorite ; (5) chlorate or chloride ; (6) acetate or sulphocyanate ; (7) phosphate or arseniate ; (8) cyanide, ferrocyanide, or ferricyanide ; (9) tartrate or citrate, etc. The following partial separation of acids may first be resorted to if necessary, and this coupled with the preliminary examination may indicate the necessity of one or other of the separations given below :—

PARTIAL SEPARATION OF ACIDS FROM EACH OTHER.

Add nitrate of calcium to the original solution (which must be neutral). Filter, wash, and treat the precipitate with acetic acid. A **CARBONATE** is here indicated by effervescence, while a **PHOSPHATE**, **ARSENATE**, and **CITRATE** (partly) pass into solution.

The residue may contain a **FLUORIDE**, **OXALATE**, **TARTRATE**, **SULPHATE**, and **BORATE**, all soluble in hydrochloric acid.

Add nitrate of silver and dilute nitric acid to the solution filtered from the nitrate of calcium precipitate. Filter, wash, then treat the precipitate with strong ammonia, and filter :—

The solution may contain a **CHLORIDE** (white), **CYANIDE** (white), **SULPHOCYANATE** (white), **FERRICYANIDE** (orange), **BROMIDE** (yellowish), and **CHROMATE** (crimson), all of which may be reprecipitated on acidulating with nitric acid.

The residue may contain an **IODIDE** (yellow—but is whitened by ammonia), **SULPHIDE** (black), and **FERROCYANIDE** (white).

The solution filtered from the nitrate of silver precipitate may contain a **TARTRATE**, **CITRATE**, **CHLORATE**, **ACETATE**, possibly a **SULPHATE**, **SULPHITE**, **NITRITE**, and a **NITRATE** originally present (as well as the nitrate added), while a **HYPOSULPHITE** and **HYPOCHLORITE** will have been destroyed.

These can again be converted into sodium salts, and the silver and calcium removed, by boiling the solution with excess of carbonate of soda, and filtering from carbonates of silver and calcium which are precipitated.

SEPARATION OF ACIDS.

(1.) Chloride, Bromide, and Iodide.

To detect the **IODIDE** add a *little* chlorine water and shake with bisulphide of carbon or chloroform (or mix with starch solution). If present, test for the **BROMIDE** in another portion of the solution, by adding a considerable excess of chlorine-water which oxidizes the iodine and leaves the bromine—which may be detected by shaking with bisulphide of carbon or chloroform. To test for the **CHLORIDE**, a portion of the solution must be evaporated to dryness (or the original solid taken), the dry residue well pounded and mixed with an excess of bichromate of potassium, in a mortar, then distilled with concentrated sulphuric acid from a small distilling flask into a test tube containing water. By this means bromine and iodine are liberated as such, while the chlorine is converted into volatile chromyl chloride CrO_2Cl_2 , which distils over, and is decomposed leaving chromic acid in solution. The contents of the test tube are boiled to get rid of bromine and iodine, and then tested with acetate of lead for chromic acid, which if present, indicates a chloride.

A method of special service for detecting a considerable quantity of a chloride in presence of a bromide or iodide, consists in boiling the mixed silver salts of the three halogens for two or three minutes with carbonate of ammonium, when the chloride is dissolved with only a trace of the bromide. On adding nitric acid in excess to the solution, chloride of silver is precipitated.

An iodide may be completely separated from a chloride by adding excess of sulphate of copper, when the following reaction occurs :—
$$2\text{CuSO}_4 + 4\text{KI} = \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$$
; the solution is filtered, and boiled to expel the remainder of the iodine.

(2.) Nitrate and Nitrite.

To detect the **NITRITE** the ordinary tests are sufficient, but as they mask the reactions of a nitrate, the nitrite must first be destroyed by boiling with urea and sulphuric acid, thus :— $2\text{HNO}_3 + \text{CO}(\text{NH}_2)_2 = \text{CO}_2 + 3\text{H}_2\text{O} + 2\text{N}_3$. The **NITRATE** may be detected in the solution by the FeSO_4 test.

(3.) Hyposulphite, Sulphate, and Sulphite.

To detect the **HYPOSULPHITE** the ordinary tests are sufficient, but they mask the reactions of the sulphite. Add chloride of barium, filter, wash with hot water, which removes hyposulphite of barium. Pour dilute hydrochloric acid on to the filter, which dissolves the sulphite of barium leaving the **SULPHATE**. Add chlorine-water to the filtrate (to convert the sulphite into sulphate), a white precipitate indicates a **SULPHITE**.

(4.) Hypochlorite and Chlorate.

Add a little caustic soda, and then sulphate of manganese, which gives a brown precipitate indicating the **HYPOCHLORITE**.
$$(\text{NaClO} + 2\text{NaHO} + \text{MnSO}_4 = \text{MnO}_2 + \text{H}_2\text{O} + \text{NaCl} + \text{Na}_2\text{SO}_4)$$
 Filter, add nitrate of silver to precipitate the chloride (avoiding excess as far as possible). Filter, and treat the solution for some time with metallic zinc and dilute sulphuric acid. This reduces the chloric acid to hydrochloric acid. Filter or decant, and add silver nitrate. A white precipitate indicates the **CHLORATE**.

(5.) Chloride and Chlorate.

Add nitrate of silver to precipitate the chloride, filter, and reduce with zinc, etc., as described above.

(6.) Acetate and Sulphocyanate.

The **ACETATE** may be detected by heating the dry substance (or residue left when the solution is evaporated to dryness), with solid arsenious anhydride when the characteristic odour of kadoyl is emitted. The **SULPHOCYANATE** may be detected by the blood-red colour with ferric chloride, after the addition of hydrochloric acid to the solution.

TABLE IX.—Continued.

(7.) Phosphate and Arseniate.

The **ARSENATE** may be detected in presence of the phosphate by the yellow precipitate formed slowly on boiling the solution with sulphuretted hydrogen and hydrochloric acid, or by Marsh's test. The **PHOSPHATE** in presence of the arseniate, by fusing the dry substance (or residue left when the solution is evaporated to dryness) in a hard glass tube with magnesium wire until the latter has become incandescent. On bringing the fused mass into water phosphuretted hydrogen is given off, which may be recognized in minute quantities by its characteristic odour.

An arseniate may be separated from a phosphate by prolonged treatment with sulphuretted hydrogen and hydrochloric acid in a boiling solution—but the process is tedious.

(8.) Cyanide, Ferrocyanide, and Ferrieyanide (as Alkaline Salts).

To detect the **CYANIDE** the solution is saturated with carbonic anhydride (which decomposes the cyanide only), and distilled. The hydrocyanic acid in the distillate may be detected by the iron test, or by the sulphocyanate reaction. To detect the **FERRO-CYANIDE**, the liquid remaining in the distilling flask is mixed with excess of ferric chloride, which precipitates the ferrocyanide as "Prussian Blue." The solution filtered from this precipitate is tested for the **FERRICYANIDE** with ferrous sulphate, which gives "Turnbull's Blue."

(9.) Tartrate and Citrate.

A **TARTRATE** is readily detected in presence of a citrate by the peroxide of hydrogen test or the silver mirror test. To detect a **CITRATE** in presence of a tartrate the latter must first be removed. To do this, mix the solution with about its own volume of a strong solution of acetate of potash dissolved in alcohol, add some acetic acid, stir well, allow to remain at rest for some time, when the whole of the tartrate is precipitated as bitartrate of potash; filter, evaporate off the alcohol, and test for the citrate with excess of baryta water or acetate of barium, both of which give with it a white precipitate.

(10.) Cyanide, Ferrocyanide, Ferrieyanide, Sulphocyanate, and Chloride, Bromide, Iodide.

To separate **CYANIDES** and **DOUBLE CYANIDES** from **HALOIDS**.—precipitate the solution with nitrate of silver, filter, and ignite the precipitate. The cyanides and double cyanides of silver are all decomposed, while the haloid compounds remain unchanged. Fuse the ignited precipitate with carbonate of soda, digest the fused mass with boiling water, filter, and test the solution for the chloride, bromide, and iodide.

TABLE X.

W signifies soluble in water.

A " insoluble in water, but soluble in nitric and in hydrochloric acid.

I " " and in both nitric and hydrochloric acid.

s " slightly soluble in the particular solvent against which it is placed.

	K ¹	NH ₄ ¹	Na ¹	Mg	Ba	Sr	Ca	Fe''	Fe'''	Ni	Co	Al	Zn
ACETATE ^s	W	W	W	W	W	W	W	W	W	W	W	W	W
ARSENATE	W	W	W	A	A	A	A	A	A	A	A	A	A
ARSENITE	W	W	W	A	W ^s -A	W ^s -A	A	A	A	A	A	—	—
BENZOATE	W	W	W	W	W	W ^s	W	A	W	W	W	W	W
BORATE	W	W	W	W ^s -A	A	A	A	A	A	A	A	A	A
BROMIDE	W	W	W	W	W	W	W	W	W	W	W	W	W
CARBONATE	W	W	W	A	A	A	A	—	A	A	A	A	A
CITRATE	W	W	W	W	A	A	W ^s -A	W	W	W	W	W	W ^s -A
CHLORIDE	W	W	W	W	W	W	W	W	W	W	W	W	W
CHLORATE ⁹	W	W	W	W	W	W	W	W	W	W	W	W	W
CHROMATE	W	W	W	W	A	W ^s -A	W ^s -A	W	—	A	A	A	W
CYANIDE	W	W	W	W	W ^s -A	W	W	W	A ^s -I	A ^s -I	A ^s -I	—	A
FLUORIDE	W	W	W	A	W ^s -A	W ^s -A	A-I ¹⁹	W	W	W	W	W&I ²⁰	W ^s -A
FORMATE	W	W	W	W	W	W	W	W	W	W ^s	W ^s -A	W	W
FERROCYANIDE	W	W	W	W	W ^s -A	W	W	I	I	I	I	W	A
FERRICYANIDE	W	W	W	W	W	—	W	W	I	I	I	—	A
HYDRATE	W	W	W	W ^s -A	W	W	W ^s	A	A	A	A	A	A
HYPOSULPHITE ¹⁰	W	W	W	W	W ^s	W	W	—	W	W	W	—	W
HYPOCHLORITE ¹³	W	W	W	W	W	W	W	—	—	—	—	—	W
IODIDE	W	W	W	W	W	W	W	W	W	W	W	W	W
NITRATE ¹⁷	W	W	W	W	W	W	W	W	W	W	W	W	W
NITRITE	W	W	W	W	W	W	W	—	—	W	—	—	—
OXALATE	W	W	W	A	A	A	A	A	A	A	A	A	A
OXIDE	W	W	W	A-I ¹⁹	W	W	W ^s	A-A ^s	A-A ^s	A	A	A-I ¹⁹	A
PHOSPHATE	W	W	W	A	A	A	A	A	A	A	A	A	A
SILICATE ²¹	W	—	W	A	A	A	A	A	A	A	A	A	A
SULPHATE	W	W	W	W	I	I	W ^s -A	W	W	W	W	W	W
SULPHITE	W	W	W	W ^s	A	A	W	W ^s -A	W ^s -A	A	A	W	W ^s -A
SULPHIDE	W	W	W	W ^s -A	W	W	W ^s -A	A	A	A ^N	A ^N	A	A
SULPHOCYANATE	W	W	W	W	W	W	W	W	W	W	W	W	W
TARTRATE	W	W	W	W ^s -A	A	A	A	W	W ^s -A	A	W	W	A
	K ¹	NH ₄ ¹	Na ¹	Mg	Ba	Sr	Ca	Fe''	Fe'''	Ni	Co	Al	Zn

* To find the solubility of any compound of one of the metals whose symbol is placed at the head of the vertical column, find the solubility of mercurous chloride, glance down the last vertical column (headed Hg₂) until insoluble in water, and only sparingly soluble in nitric acid.

NOTES TO TABLE X.—*Solubility Table.*

1. All the ordinary salts of the alkali metals are soluble.
2. As salts of lead are precipitated by hydrochloric acid, the solubility of those salts which are insoluble in water, but soluble in acids are marked "N" signifying that they give a clear solution with nitric acid.
3. Bismuth salts are as a rule decomposed by water giving basic compounds soluble in nitric and hydrochloric acids.
4. Antimony salts are as a rule decomposed by water giving basic compounds soluble in acids.
5. Very few salts of arsenic are known.
6. As salts of silver are precipitated by hydrochloric acid, those salts which are insoluble in water, but soluble in acids are marked "N" signifying that they give a clear solution with nitric acid.
7. The same note as 6 applies to mercurous salts.
8. Probably all normal acetates are soluble in water, but basic acetates often are not.
9. Probably all chlorates are soluble in water.
10. Hyposulphites are decomposed by acids with precipitation of sulphur.
11. Hyposulphite of silver is white, but changes rapidly, becoming yellow, orange, brown, and finally black— $\text{Ag}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = \text{Ag}_2\text{S} + \text{H}_2\text{SO}_4$. It is soluble in excess of alkaline hyposulphites.
12. A mercurous salt gives a black precipitate, with a soluble hyposulphite, of mercurous sulphide— $\text{Hg}_2(\text{NO}_3)_2 + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = \text{Hg}_2\text{S} + \text{H}_2\text{SO}_4 + 2\text{NaNO}_3$.
13. Ordinary hypochlorites always contain chlorides in addition.
14. A manganese salt gives a brown precipitate of hydrated manganese peroxide with a hypochlorite— $\text{MnCl}_2 + \text{NaClO} + 2\text{NaHO} = \text{MnO}_2 \cdot \text{H}_2\text{O} + 3\text{NaCl}$.
15. Hypochlorite of silver is soluble, but decomposes spontaneously into chlorate (soluble) and chloride (insoluble)— $3\text{AgClO} = \text{AgClO}_3 + 2\text{AgCl}$.
16. A cupric salt when mixed with a soluble iodide, gives a precipitate consisting of a mixture of cuprous iodide and free iodine— $2\text{CuSO}_4 + 4\text{KI} = \text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$.
17. Probably all nitrates are soluble in water.
18. A solution of a mercurous salt when mixed with a nitrite, gives a grey precipitate of metallic mercury— $\text{Hg}_2(\text{NO}_3)_2 + \text{KNO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{KNO}_3 + 2\text{Hg}$.
19. The native compound is insoluble in water and acids.
20. After ignition it is insoluble in acids.
21. Most natural silicates are insoluble in water and acids, but artificial silicates are often soluble in dilute acids. Such solutions when concentrated yield a gelatinous mass of silica and a soluble salt of the metal.
22. Soluble in aqua regia only, or in a mixture of hydrochloric acid and chlorate of potash.

REACTIONS AND PROPERTIES
OF SOME OF THE MORE
IMPORTANT ORGANIC SUBSTANCES,
WITH TABLES FOR THEIR DETECTION.

Alkaloids.

The alkaloids form a series of natural principles, mostly derived from vegetable sources. They always contain nitrogen and are more or less closely allied to ammonia. Some contain carbon, hydrogen, and nitrogen only while others contain oxygen in addition. The former are as a rule volatile, while the latter generally, but not always, decompose when heated. The alkaloids frequently have a bitter taste and generally have a powerful physiological action, many of them being violent poisons. They neutralize acids, forming as a rule crystallizable salts. Most of them are sparingly soluble in water, but readily dissolve in alcohol. There are certain general reagents which react in a similar manner with all alkaloids, among which are the following :—

1. **Chloride of platinum**—combines with the hydrochlorates of the alkaloids, forming compounds analogous to the double chloride of ammonium and platinum $2\text{NH}_4\text{Cl}$, PtCl_4 . They are best obtained (if not insoluble) by evaporating the mixed solution of chloride of platinum and hydrochlorate of the alkaloid to dryness, and adding alcohol to the residue.
2. **Solution of iodine in iodide of potassium**, (best decinormal solution)—throws down all the alkaloids from solutions of their salts in the form of yellow, brown or reddish-brown precipitates consisting of their polyiodides. If these precipitates are well washed, and then evaporated to dryness on a water bath with excess of sulphurous acid, the pure sulphate of the alkaloid remains.
3. **Solution of iodide of mercury in iodide of potassium***—throws down all the alkaloids from their solutions in the form of white or yellowish-white precipitates.
4. **Solution of the iodides of cadmium and potassium**†—precipitates the alkaloids after their solutions have been acidulated with sulphuric acid. The precipitates are all white and amorphous at first, but some of them become crystalline on standing.
5. **Solution of the iodides of bismuth and potassium**—gives with most (but not all) alkaloids flocculent orange coloured precipitates.
6. **Phospho-molybdic acid**‡—precipitates all the alkaloids, even when their quantity is very minute. The precipitates are bright yellow, ochreous, or brownish-yellow in colour, and have an analogous composition to phospho-molybdate of ammonium. On warming the precipitate with caustic potash or soda, the alkaloid separates in the free state, and may be removed by extracting the solution with ether, amyl alcohol, benzol, &c.
7. **Metatungstic acid (or a solution of tungstate of soda) to which phosphoric acid has been added**—precipitates all the alkaloids from their solutions. The precipitates are white and flocculent, and the reaction is very delicate. To obtain the free alkaloid from the precipitate the latter is digested with lime or baryta, when insoluble phospho-tungstate of lime or baryta and the alkaloid separate.
8. **Picric acid**—throws down nearly all the alkaloids in the form of yellow precipitates, insoluble in excess of the precipitant.

* A solution of iodide of potassium to which mercuric chloride has been added until the precipitate first formed just ceases to be redissolved on shaking.

† Prepared by saturating a boiling concentrated solution of iodide of potassium with iodide of cadmium, and adding an equal volume of iodide of potassium.

‡ Prepared as follows :—A boiling solution of ordinary molybdate of ammonium is precipitated with phosphate of soda; the precipitate is well washed, suspended in water, and warmed with a solution of carbonate of soda until it is completely dissolved. The solution is evaporated to dryness, the residue ignited, and if reduction has taken place it is moistened with nitric acid and ignited again. The product is warmed with water, and dissolved by adding nitric acid in considerable excess (one part of the residue should make ten parts of solution).

QUININE— $C_{20}H_{24}N_2O_2, 3H_2O$

Occurs in the bark of the cinchona tree along with cinchonine. The free alkaloid is crystalline, sparingly soluble in cold—more readily in hot water. It is easily soluble in alcohol and chloroform, but less so in ether. Solutions both of the free alkaloid and of its salts have an intense bitter taste.

1. Solutions of quinine salts which contain an oxygen acid (especially the sulphate) show a very characteristic blue fluorescence.
2. Caustic potash and soda, ammonia, and the carbonates and bicarbonates of potash and soda precipitate the free alkaloid from solutions of its salts. The precipitate is white and amorphous when first formed, but becomes crystalline after some time.
3. On adding chlorine-water and then excess of ammonia, solutions of quinine salts give an emerald-green colour. If, before adding ammonia, a few drops of ferrocyanide of potassium are added, a deep red coloration is produced. These reactions are delicate and highly characteristic.

CINCHONINE— $C_{19}H_{22}N_2O$

Accompanies quinine in cinchona bark. The free alkaloid is crystalline, very sparingly soluble in cold and in hot water. It is more readily soluble in alcohol, and also dissolves in ether and chloroform. It has a bitter taste. When heated cautiously the alkaloid sublimes unchanged.

1. Caustic potash or soda, ammonia, and the carbonates and bicarbonates of potash and soda precipitate the free alkaloid from solutions of its salts. The precipitate does not present a crystalline appearance unless produced in very weak solution.
2. On adding ferrocyanide of potassium to a neutral solution of a salt of cinchonine, a flocculent precipitate of the ferrocyanide of the alkaloid is thrown down. If this is warmed with a slight excess of the precipitant it redissolves, and on cooling separates in brilliant golden yellow scales or needles.

STRYCHNINE— $C_{21}H_{22}N_2O_2$

Occurs in the different varieties of *strychnos*, especially in *nux vomica*, the *St. Ignatius bean*, and in *false angostura* bark. It is always accompanied by the alkaloid brucine. The free alkaloid is crystalline, and has an intensely bitter taste (appreciable in a solution containing 1 part of the alkaloid in 700,000 of water). It dissolves readily in boiling chloroform, benzol, and amyl alcohol. But it is almost insoluble in cold water, and even boiling water dissolves only minute quantities.

Its salts are as a rule insoluble in water, and all have a very bitter taste, and like the free alkaloid are extremely poisonous.

1. Caustic potash or soda and their carbonates produce a white crystalline precipitate with solutions of the salts of strychnine. Ammonia gives the same precipitate, but it is soluble in excess. After some time, however, the free alkaloid again separates out from the ammoniacal solution in crystalline needles.
2. If strong sulphuric acid is added to a salt of strychnine, or to the free base, and then a fragment of bichromate of potash added, a magnificent violet colour is produced. The reaction is delicate and highly characteristic.

3. Sulphocyanate of potassium produces a white precipitate with solutions of strychnine salts, consisting of the sulphocyanate of the alkaloid. The precipitate is somewhat soluble in excess of the precipitant, and only appears after some time in dilute solutions.
4. Strong chlorine-water produces in solutions of strychnine salts a white precipitate, soluble in ammonia to a colourless fluid.

BRUCINE— $C_{23}H_{26}N_2O_4 \cdot 4H_2O$

Accompanies strychnine in nature. The free alkaloid is colourless and crystalline. It is far more soluble in water than strychnine. It dissolves very readily in alcohol, amyl alcohol, chloroform, and benzol, but it is almost insoluble in ether. When cautiously heated it first loses its water of crystallization, and then sublimes unchanged. Both the free alkaloid and its salts have a strong bitter taste.

1. Caustic potash and soda, and their carbonates precipitate the free alkaloid from solutions of its salts. Ammonia behaves similarly, but the precipitate when first produced redissolves in excess of the precipitant, but is thrown down again after the lapse of some time.
2. Strong nitric acid dissolves brucine and its salts, forming a blood-red solution which becomes yellow on heating. On adding stannous chloride or sulphide of ammonium (either to the diluted or undiluted fluid) it acquires an intense violet colour.
3. Concentrated sulphuric acid dissolves brucine and its salts to a faint rose coloured solution. The smallest trace of nitric acid causes the development of a transient red colour, eventually changing to yellow. This reaction is delicate and highly characteristic.
4. Chlorine-water when added to a solution of a brucine salt colours it red. On addition of ammonia the solution becomes yellowish brown.
5. Sulphocyanate of potassium reacts as with strychnine salts.

MORPHINE— $C_{17}H_{19}NO_3 \cdot H_2O$

Occurs in the juice of the poppy, along with several other less important alkaloids and meconic acid. The free alkaloid is crystalline, has a bitter taste, is sparingly soluble in cold, but more readily in hot water. It is also soluble in alcohol, and amyl alcohol, but scarcely dissolves in ether or chloroform.

1. Caustic potash and soda, also ammonia, as well as the carbonates and bicarbonates of potash and soda precipitate the free alkaloid from solutions of its salts (if not too dilute). The precipitate dissolves easily in excess of potash or soda, but is much more sparingly soluble in ammonia.
2. Iodic acid is decomposed by solutions of morphine and its salts, with separation of iodine. The latter may be detected by the violet colour which it imparts to chloroform or bisulphide of carbon, or by the blue colour which it strikes with starch paste.
3. Neutral ferric chloride gives a deep indigo-blue colour with (concentrated) neutral solutions of salts of morphine. This reaction is characteristic.
4. Strong sulphuric acid when warmed with the free alkaloid or its salts gives no colour, but on adding to the cooled solution a minute quantity of nitric acid, it assumes a red colour (heating promotes the reaction). If a fragment of bichromate of potash is now placed in the liquid, it acquires an intense mahogany-brown colour.

TABLE XI.

Examination for a Single Alkaloid in a Solution (after Fresenius).

(It is presupposed that the alkaloids are in concentrated aqueous solution as salts, and free from any substances which would obscure or modify the reactions.)

(1.) Treat the solution with caustic potash until it is just alkaline. Stir the mixture vigorously, and allow to stand.

RESULT.	SHOWS PRESENCE OF :—	CONFIRMATORY TESTS.
No precipitate is formed.	(possibly) ATROPINE	(1) A peculiar odour of flowers is produced when atropine and its salts are heated with sulphuric acid, or chromic acid. (2) Physiological action on the eye (dilation of the pupil).
	NICOTINE	(1) Hydrochloric acid gives when evaporated to dryness with the ethereal extract obtained from the caustic potash solution, an <i>amorphous</i> precipitate of the hydrochlorate.
	CONIINE	(1) Hydrochloric acid gives when evaporated to dryness with the ethereal extract obtained from the caustic potash solution, a <i>crystalline</i> precipitate of the hydrochlorate. (2) Solutions of coniine and its salts when boiled (especially if free acid is present) become coloured red, then violet, green, blue, and finally brownish.
A precipitate is produced, but disappears on adding an excess of the reagent.	MORPHINE	(1) Iodic acid causes a separation of iodine. (2) Neutral ferric chloride gives a blue colour (only with neutral and fairly concentrated solutions of the alkaloid).
	ATROPINE	(1) No separation of iodine occurs on the addition of iodic acid. (2) See above.

(2.) Add two or three drops of dilute sulphuric acid, then a saturated solution of bicarbonate of soda until the mixture is just neutral, stir well, and allow it to stand for half-an-hour.

A precipitate is formed.	CINCHONINE	<p>(1) Ammonia added in excess, then a small quantity of ether, and the liquid shaken—the precipitate first formed <i>does not</i> dissolve.</p> <p>(2) Cinchonine, when cautiously heated, fuses, then evolves white fumes which condense, giving crystalline needles.</p> <p>(3) Ferrocyamide of potassium gives with a neutral solution of the alkaloid a white ppt. soluble in excess on heating. On allowing the solution to cool golden-yellow crystals separate out.</p>
	NARCOTINE	<p>(1) Ammonia added in excess, then a small quantity of ether, and the liquid shaken—the precipitate first formed <i>dissolves</i> (difference from cinchonine).</p> <p>(2) On the addition of chlorine-water and a drop or two of ammonia a <i>deep red</i> solution is produced.</p>
	(possibly) QUININE	<p>(1) Ammonia added in excess, then a small quantity of ether, and the liquid shaken—the precipitate first formed <i>dissolves</i>.</p> <p>(2) On the addition of chlorine-water and then excess of ammonia an <i>emerald-green</i> solution is produced. If ferrocyamide of potassium is added before the ammonia, the solution becomes coloured mahogany-brown.</p>

(3.) Evaporate some of the solution to dryness on a watch glass (or if the substance is solid use it direct), and add concentrated sulphuric acid.

A <i>rose-red coloration</i> is obtained which becomes intensely red on addition of nitric acid.	BRUCINE	<p>(1) Chlorine-water (or better, the gas) colours solutions of brucine salts red. On adding ammonia the colour becomes red-brown.</p> <p>(2) Nitric acid gives a solution at first scarlet to blood-red—then yellow. If stannous chloride is added to this solution it becomes coloured violet.</p>
A <i>yellowish solution</i> is obtained which gradually turns yellowish-red, blood-red, and finally crimson.	VERATRINE	<p>(1) The alkaloid when mixed in a mortar with cane sugar and concentrated sulphuric acid becomes at first yellow, then grass-green, and finally blue.</p>

<p>A <i>yellow solution</i> is obtained which does not change on standing. Add a fragment of bichromate of potash <i>A.</i>—A deep blue colour is produced.</p>	STRYCHNINE	<p>(1) Solutions of strychnine salts give a white crystalline precipitate with potassium sulphocyanate. (2) Bitter taste of very dilute solutions. (3) Physiological action.</p>
	QUININE	<p>(1) Solutions of the acid salts of quinine containing oxygen acids are fluorescent. (2) Solutions of quinine salts when mixed first with chlorine-water, and then with ammonia, become emerald-green. If ferrocyanide of potassium is added before the ammonia, the solution becomes coloured mahogany-brown.</p>
<p>A <i>reddish-brown coloration</i> is produced which changes to a purple on the addition of a drop of bromine water.</p>	DIGITALIN*	<p>On warming an aqueous solution of digitalin with a few drops of phospho-molybdic acid, a beautiful green colour appears, which on addition of a little ammonia changes to blue.</p>
	PICROTOXIN*	<p>(1) Picrotoxin when moistened with concentrated nitric acid, dried on the water bath, then moistened with the smallest possible amount of sulphuric acid, and finally mixed with excess of strong caustic potash solution gives a pale red or reddish-yellow colour. (2) On warming an alkaline solution of picrotoxin with Fehling's solution, a precipitate of red oxide of copper is formed.</p>
<p>A <i>blood-red colour</i> is produced.</p>	SALICIN*	<p>(1) Ferric chloride colours solutions of salicin a pale brown, but on boiling, the mixture becomes colourless, while a dull yellow precipitate is formed. (2) On heating a solution of salicin with nitrate of silver to which excess of ammonia has been added and either caustic potash or soda, the silver is reduced, and a brilliant mirror of metallic silver is formed.</p>

The above scheme does not take into account the rarer alkaloids. If one of them is suspected, and no satisfactory result can be obtained by working according to the scheme, separate portions of the substance or solution should be tested for each of the rarer alkaloids. The following Table will facilitate the examination.

* These substances are not alkaloids, as they contain no nitrogen, but on account of their physiological actions they are usually classed with the latter.

TABLE XII.

Reactions of Alkaloids.

ALKALOID.	STRONG SULPHURIC ACID.	STRONG NITRIC ACID.	OTHER CHARACTERISTIC REACTIONS.
MORPHINE	Dissolves to a colourless solution. When warmed at 100°C for half-an-hour, the addition of a small fragment of nitrate of potash gives a beautiful blue to red-violet colour, which soon passes to a blood-red, and then slowly fades.	Coloured at first blood-red changing gradually to yellow. The yellow solution suffers no change on addition of stannous chloride or sulphide of ammonium.	(1) Solutions of morphine salts liberate iodine from iodic acid. (2) Solutions of morphine salts give, with neutral ferric chloride, a blue colour. (3) Fröhde's reagent* gives a deep violet, then blue, dirty green, and finally a faint red colour. (4) The alkaloid is soluble in excess of caustic potash.
STRYCHNINE	Dissolves to a colourless solution. On adding to this a fragment of bichromate of potash, streaks of purple are produced.	Dissolves to a yellow solution.	(1) Solutions of strychnine salts give a white crystalline precipitate with KCNS. (2) Bitter taste if very dilute solutions. (3) Physiological action.
QUININE	Dissolves to a colourless or faint yellow liquid. When heated the mixture becomes yellow, then brown.	Dissolves to a colourless fluid, becoming yellowish when heated.	(1) Solutions of the acid salts of quinine (with oxygen acids) are fluorescent. (2) Solutions of quinine salts when mixed first with chlorine-water and then with ammonia, become emerald-green. If ferrocyanide of potassium is added before the ammonia, the solution becomes coloured mahogany-brown.
CINCHONINE	Dissolves to a colourless fluid, which when heated, first becomes brown, then black.		(1) Cinchonine when cautiously heated, fuses, then evolves white fumes, which condense, giving crystalline needles. (2) Neutral solutions of cinchonine salts give a white precipitate with ferrocyanide of potassium, soluble when cautiously heated with excess of the ferrocyanide, but separating in golden-yellow crystals as the solution cools.

* Fröhde's reagent is prepared by dissolving pure molybdic acid or molybdate of soda in concentrated sulphuric acid. One cubic centimetre of the solution should contain five milligrams of the salt. The solution should be prepared immediately before use, and ought to be colourless.

ACONITINE	Dissolves to a colourless or yellow fluid, becoming brown when heated.	Dissolves to a yellow fluid.	(1) Physiological action.
BRUCINE	Dissolves to a faint rose-coloured or colourless solution; coloured transiently red, and eventually yellow, by a trace of nitric acid.	Coloured scarlet to blood-red, then yellow. If stannous chloride or sulphide of ammonium are added to this solution it becomes coloured violet.	(1) Chlorine-water (or better the gas) colours solutions of brucine salts red. On adding ammonia the colour becomes red-brown.
CONIINE	Dissolves to a colourless solution, becoming charred on heating.	Little or no immediate change.	(1) Odour, volatility, and alkaline reaction of the free alkaloid. (2) Gives a <i>crystalline</i> hydrochlorate. (3) Solutions of coniine salts when boiled (especially if free acid is present) become coloured red, then violet, green, blue, and finally brownish.
ATROPINE or (DATURINE)	Dissolves to a colourless fluid, becoming brown on warming.	Dissolves to a colourless fluid. (If the alkaloid is evaporated to dryness with fuming nitric acid and alcoholic potash added to the colourless residue, a violet colour is produced, which changes to cherry-red. The reaction is characteristic.)	(1) A peculiar odour of flowers is produced when atropine or its salts are heated with sulphuric acid, or chromic acid. (2) Physiological action on the eye (dilation of the pupil).
NICOTINE	Dissolves to a colourless solution, becoming charred on warming.	Dissolves to a red solution.	(1) Odour, volatility, and alkaline reaction of the free alkaloid. (2) Gives an amorphous hydrochlorate.
VERATRINE	Dissolves to a yellow liquid, becoming deep red when heated.	The alkaloid agglutinates into resinous lumps, which afterwards dissolve slowly.	(1) The alkaloid when mixed in a mortar with cane sugar and concentrated sulphuric acid becomes at first yellow, then grass-green, and finally blue.

TABLE XII.—Continued.

ALKALOID.	STRONG SULPHURIC ACID.	STRONG NITRIC ACID.	OTHER CHARACTERISTIC REACTIONS.
CODEINE	Dissolves to a colourless fluid, becoming slightly blue when heated. On addition of ferric chloride—deep blue. On addition of sugar—purple red.	Dissolves to a brown-red colour.	(1) Fröhde's reagent dissolves codeine at first with a yellow colour, which rapidly becomes deep green, and finally blue. (2) When heated with water, codeine melts and forms oily drops. (3) Dissolved in chlorine-water, codeine gives a colourless solution, which becomes yellow-red on adding ammonia.
THEBaine	Dissolves, giving an immediate blood-red colour. The solution gradually becomes yellow-red.		* (1) Fröhde's reagent dissolves thebaine, forming a blood-red solution. (2) A solution of the alkaloid in chlorine-water becomes coloured; an intense red-brown on adding ammonia. (3) Sulphuric acid containing nitric acid is coloured by the alkaloid dark-red or orange.
NARCEINE	Dissolves, forming a greyish-brown solution, which gradually becomes blood-red (rapidly when heated).	Dissolves immediately, giving a yellow solution.	(1) Fröhde's reagent dissolves narceine, giving at first a brown-green colour, which soon becomes olive-green, and finally blood-red. (2) Iodine-water colours the solid alkaloid an intense blue. (3) The alkaloid when stirred with chlorine-water, and then a drop or two of ammonia, gives a deep red solution.
PAPaverine	Dissolves to a colourless or slightly yellow solution, which on warming becomes dark violet.		(1) Fröhde's reagent dissolves papaverine in the cold, giving a green colour. On warming, the solution shows a transient blue, and finally a cherry-red colour. (2) Iodine-water colours the alkaloid dark-red, then brick-red, and then dark-red again. (3) With chlorine-water and ammonia the alkaloid gives at first a red-brown, and finally nearly a black-brown solution.

NARCOTINE	Dissolves to a greenish-yellow liquid, becoming pure yellow. On warming, the solution becomes orange-red, bluish-violet or purple, and finally dirty reddish-violet.	Dissolves on warming with evolution of nitrous fumes, forming a reddish-yellow solution. On heating strongly, more nitrous fumes are evolved, and the liquid becomes yellow.	(1) Heated with concentrated sulphuric acid until red, and afterwards mixed with ferric chloride, a violet coloration is at first produced, gradually becoming cherry-red. (2) Fröhde's reagent gives the same reaction as with papaverine. (3) Chlorine-water added to a solution of narcotine gives a yellow colour, slightly inclining to green. On the addition of ammonia a yellowish-red colour is produced.
EMETINE	Dissolves to a colourless solution.		(1) Fröhde's reagent colours the alkaloid deep chocolate-brown. If a drop of strong hydrochloric acid is added quickly to the mixture, a blue colour is immediately produced, which soon passes into a green. (2) Physiological action (emetic).
PHYSOSTIGMINE	Dissolves with a yellow colour, or to a colourless solution.	Dissolves, forming a yellow solution.	(1) Bleaching powder colours a solution of the alkaloid at first red, but on adding more of the reagent the colour disappears. (2) Bromine-water produces a yellow precipitate in an aqueous solution of the base. (3) Physiological action (contraction of the pupil of the eye).
CURARINE	Dissolves with a pale violet colour. The solution becomes very gradually dirty red, and then rose-red.	Dissolves, forming a purple-red solution.	(1) Behaves with concentrated sulphuric acid and bichromate of potash, like strychnine, but the colour is more permanent. (2) Physiological action (paralysis of the voluntary muscles.)
DELPHININE	Dissolves at first with a brown colour, which gradually becomes deep red-brown. On addition of a little bromine-water, and stirring, the brown solution becomes at first violet, then cherry-red, and finally blood-red.		(1) Fröhde's reagent dissolves the alkaloid at first, forming a dark-brown solution, which rapidly becomes blood-red, and finally dirty red. (2) The solid alkaloid when stirred with strong sugar syrup and a drop of sulphuric acid added, a brown colour is produced, which soon passes into a green.

Reactions of the Chief Constituents of Healthy and Morbid Urine.

Human urine when freshly voided is an amber coloured liquid, having a faint acid reaction, a sp. gr. about 1020, and a peculiar characteristic smell. It contains about 95·5 per cent. of water, and 4·5 per cent of solids.

The following table shows the names and average amount of the different solid substances present (Roberts) :—

EXTRACTIVES	Urea,	2·157
	Uric acid,	·036
	Creatine,	·653
	Creatinine,	
	Ammonia,	
	Hippuric acid,	
	Xanthine,	
	Hypoxanthine,	
	Sarcine,	
	Pigments, etc.,	
FIXED SALTS	Chlorine,	·457
	Sulphuric acid,	·131
	Phosphoric acid,	·209
	Potash,	·140
	Soda,	·719
	Lime,	·011
	Magnesia,	·012
						<hr/> 4·525

The colour, sp. gr., reaction, and odour of *normal* urine are subject to considerable variations, depending on the nature of the food taken, the amount of liquid consumed, the period at which the urine is voided, the action of certain drugs, etc. Morbid urine may either contain abnormally large proportions of the above constituents or else bodies, such as albumen, sugar, spermatozoa, fat, cystine, pus, etc.

UREA— $\text{CO}(\text{NH}_2)_2$

Crystallizes in colourless four-sided prisms. It has a cooling bitter taste like saltpetre. It dissolves readily in water and alcohol. It combines with acids, bases, and salts.

1. A concentrated solution of urea is precipitated by strong nitric acid as the nitrate of urea, $\text{CO}(\text{NH}_2)_2, \text{HNO}_3$, in white glistening plates or scales.

A strong solution of oxalic acid throws down the oxalate— $2\text{CO}(\text{NH}_2)_2, \text{C}_2\text{H}_2\text{O}_4$.

2. A dilute solution of urea is precipitated by mercuric nitrate (compounds of mercuric oxide and urea being formed). The precipitate is white and flocculent, soluble in a small quantity of common salt solution, but again precipitated on addition of mercuric nitrate.
3. A solution of urea is decomposed by nitrous acid (or a solution of potassium nitrite, to which a drop or two of nitric acid have been added). Effervescence occurs, and the escaping gases consist of nitrogen and carbonic anhydride. The latter can be detected by lime-water— $\text{CO}(\text{NH}_2)_2 + \text{N}_2\text{O}_3 = 2\text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O}$.

4. Urea is decomposed by potassium hypobromite (made by adding bromine to cold caustic potash solution until it ceases to be decolorized), with effervescence, into the same products— $\text{CO}(\text{NH}_2)_2 + 3\text{KBrO} = \text{CO}_2 + 2\text{H}_2\text{O} + \text{N}_2 + 3\text{KBr}$. Only the nitrogen escapes, as the carbonic anhydride is retained in solution as potassium carbonate.
5. Dry urea when cautiously heated in a dry test tube until it melts, and just begins to disengage ammoniacal fumes, is converted into biuret. On dissolving the biuret in water, adding excess of caustic soda, and then drop by drop, a dilute solution of copper sulphate, the solution becomes coloured first red, then red-violet, and finally violet, (biuret reaction).

URIC ACID— $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$.

Pure uric acid is a white powder, very insoluble in water (1 part dissolves in 14,000—15,000 of cold, and in 1,800—1,900 of boiling water). It is insoluble in alcohol and ether, but dissolves in caustic potash or soda, and in solutions of their carbonates and phosphates. It is insoluble in ammonia. It forms two classes of salts, acid and normal, according as one or two of its hydrogen atoms are replaced by metals. From solutions of these it is precipitated by acids.

1. The most characteristic reaction of uric acid is based upon the production of *murexide*.

A few grains of solid uric acid, or a urate, are heated with strong nitric acid, when a brisk effervescence occurs. On evaporating to dryness on a water bath, and exposing the residue (colour either yellow or brick-red) to the fumes of ammonia, a violet colour is produced (due to the production of *murexide* or purpurate of ammonium— $\text{C}_8\text{H}_4\text{NH}_4\text{N}_5\text{O}_6$).

HIPPURIC ACID— $\text{C}_9\text{H}_9\text{NO}_3$

Crystallizes in white four-sided prisms. Slightly soluble in cold, more readily in hot water. Soluble with ease in alcohol; also soluble, though less easily, in ether. It combines readily with bases to form salts, which for the greater part are soluble. When boiled with hydrating agents it is converted into glycocoll and benzoic acid— $\text{C}_9\text{H}_9\text{NO}_3 + \text{H}_2\text{O} = \text{C}_7\text{H}_6\text{O}_2 + \text{C}_2\text{H}_5\text{NO}_2$.

1. Solid hippuric acid, when gently warmed in a test tube, melts to an oily liquid, then grows red, and is decomposed, giving a sublimate of benzoic acid, and an odour like bitter almonds (benzo-nitrile).

ALBUMEN.

Albumen in urine can be detected as follows :—

1. The urine is boiled in a tube, and a few drops of strong nitric acid are added, (so that the mixture has a well marked acid reaction). The presence of albumen is indicated by a flocculent precipitate. (This test is open to the objection that urates may be also precipitated, and also it is not very delicate.)
2. Concentrated nitric acid is poured cautiously down the side of a test tube containing the urine. If albumen is present, a sharply defined cloudy ring appears at the junction of the two fluids (Heller).
3. The urine is acidulated strongly with acetic acid, then about an equal part of a saturated solution of common salt is added, and the mixture boiled. The presence of albumen is indicated by a flocculent precipitate.
4. The urine is acidulated strongly with acetic acid, and a few drops of ferrocyanide of potassium are added. A thick white precipitate is then produced if albumen is present.
5. On adding albuminous urine to a solution of picric acid, (saturated in the cold) a white precipitate is produced.

6. The urine is saturated in the cold with crystallized sulphate of magnesium, then filtered from the undissolved portion, strongly acidulated with acetic acid, and boiled. A flocculent precipitate indicates albumen.*

BLOOD.

Blood in urine generally colours the excretion red, brown, or black, and causes it to be turbid.

1. On examining a test tube full of the urine placed before the slit of the spectroscope two well defined absorption bands are seen.
2. The urine when boiled gives a precipitate of albumen, which is coloured more or less brown.
3. The urine is made strongly alkaline with caustic soda, and boiled. The haemoglobin of the blood is converted into haematin, which adheres to the precipitated earthy phosphates colouring them brown. (This is a very delicate reaction.)
4. Small quantities of blood in urine are precipitated by tannin. The precipitate may be collected, dried in the air, and examined as described at page 89 (under "Blood," test 3).

BILE.

Urine containing biliary matters is coloured yellow, brown, or green, and froths when shaken. The following tests for bile *pigments* may be employed :—

1. A few cubic centimetres of strong nitric acid (having a yellow colour) are placed in a test tube ; the latter is then held in a slanting position, and the urine is carefully poured down the side of the tube, so that it forms a distinct layer above the nitric acid. At the point of junction of the two fluids, a play of colours becomes apparent. If this at any time is green, biliary matters are present (Gmelin).
2. On adding to the suspected urine a few drops of tincture of iodine, an emerald-green colour is produced (Trousseau and Dumontpallier). Bromine-water may be substituted for iodine (Maly).

Bile *acids* may be detected thus :—

A few cubic centimetres of the urine are placed in a test tube along with a fragment of loaf sugar. A small quantity of concentrated sulphuric acid is then poured carefully down the side of the tube, so that it forms a distinct layer at the bottom. At the line of contact of the two liquids a deep purple colour is produced, after a few minutes, if bile acids are present (Pettenkofer and Harley).

SUGAR.

Grape Sugar (dextrose)— $C_6H_{12}O_6$ —occurs abundantly in the urine of patients suffering from diabetes. In such cases large quantities of urine are often voided.

The following tests may be employed :—

1. The urine is made strongly alkaline with caustic potash or soda, and then boiled for some time. If the colour darkens *considerably* sugar is present (Moore and Heller). Normal urine darkens slightly when boiled with alkalies, and the presence of lead in the latter also causes them to give a dark colour with urine ; so that this test is not very trustworthy in doubtful cases.
2. As in 1, the urine is made strongly alkaline with caustic potash or soda, then rather dilute sulphate of copper solution is added drop by drop, (the mixture being shaken vigorously all the time), until a very little of the precipitated hydrate of copper remains undissolved. On

* Globulin behaves like albumen in all the tests given with the exception of this one.

warming, a yellow or red precipitate of cuprous oxide separates, (if sugar is present) *before* the mixture boils. The heating is then interrupted, and the reduction proceeds by itself (Trommer).*

3. The urine is made alkaline as before, a solution of nitrate of bismuth is then added until a fair amount of precipitate is produced, and the mixture warmed. The precipitate darkens rapidly if sugar is present, and the liquid itself becomes brown (Böttger).
4. The urine is mixed with a few crumbs of German yeast. A test tube is filled to the brim with the mixture, then closed with the thumb, and inverted in a dish or basin containing more of the urine. The tube and basin are then set aside in a warm place (say on the mantel-piece). If sugar is present, fermentation soon occurs and carbonic anhydride is formed, which gradually displaces the urine in the tube (Fermentation test).†

Urinary Sediments and Calculi.

Very frequently freshly voided urine is cloudy, or rapidly becomes so on standing, and eventually deposits a sediment. The sediment is caused by the separation of some normal or a bnormal constituent—the former in excess of normal amount. Should the deposition occur gradually within the bladder or kidney, it not unfrequently happens that the separated particles become agglomerated into a hard mass, which is called a “stone” or “calculus.” *Urinary sediments* may consist of the following :—

NON-ORGANISED.	{	<ol style="list-style-type: none"> 1. Uric acid and urates. 2. Phosphate of lime. 3. Oxalate of lime. 4. Phosphate of ammonia and magnesia. 5. Carbonate of lime. 6. Cystine. 7. Fat globules.
ORGANISED.	{	<ol style="list-style-type: none"> 8. Epithelium. 9. Mucus. 10. Pus. 11. Blood. 12. Spermatzoa. 13. Micro-organisms. 14. Casts of uriniferous tubes. 15. Hydatids.

and a few other bodies, such as indigo, xanthine, leucine, tyrosine, hippuric acid, sulphate of lime, phosphate of magnesia, etc. *Urinary calculi* contain the same substances as those present in non-organised sediments, with the exception of hippuric acid and tyrosine.

* Instead of applying the “reduction test” as above, the following modification may be used if greater certainty is desired :—Fill a test tube to the depth of $\frac{3}{4}$ of an inch or so with “Fehling’s solution” (p. 84, foot note), heat until it begins to boil, and then add a drop or two of the suspected urine. If it is ordinary diabetic urine, the mixture after an interval of a few seconds, will *suddenly* turn to an intense opaque-yellow colour, and in a short time an abundant yellow or red sediment falls to the bottom. If, however, the quantity of sugar present is small, the suspected urine is added more freely, but *not beyond a volume equal to that of the test employed*. In this latter case it is necessary to raise the mixture once more to the boiling point. It is then allowed to cool slowly. If no suboxide has been thrown down when it has become cold, then the urine may with certainty be pronounced sugar free—(Roberts).

† This is often used by physicians as a quantitative test—the difference in Sp. Gr. before and after fermentation roughly representing the amount of sugar per ounce—(Roberts).

TABLE XIII.

Examination of Morbid Urine.

Colour—varies greatly. It may be the same as that of normal urine, or blood-red, brown or brownish-black (blood, etc.) ; also yellowish-green or brownish-green (bile).

Odour—variable.

Specific gravity—variable. Low density (1005—1015). A high density (above 1025) may indicate sugar as well as an excess of urea, etc. *Reaction*—variable. It may be alkaline from the decomposition, within the bladder, of urea producing ammonia (the urine is then turbid from precipitation of phosphates, and usually smells of ammonia). It may also be alkaline from the presence of fixed alkalies (caustic potash or soda), and it may be acid.*

Substances present.—The most important substances which may be present in morbid urine are sugar (diabetes), blood (various affections), albumen, casts, etc., (Bright's disease), bile (jaundice), hooklets (hydatid disease), fat, cystine, pus, spermatozoa, etc. Morbid urine may, however, only differ from the healthy excretion in containing excessive quantities of some of its normal constituents, such as uric acid and urates (gouty affections), urea, earthy phosphates, etc. These often separate as a sediment. As a rule the physician merely tests for some special substance, which from the symptoms of the case he suspects to be present. Should it be necessary, however, the following scheme may be employed :—

Allow any sediment that may be present in the urine to settle. Decant, and filter :—			
Residue	Filtrate.		
Examine by Table XIV, p. 76.	Heat to boiling.† If a precipitate appears, allow to cool, and add strong nitric acid. A permanent flocculent precipitate† may indicate :—		
	1. ALBUMEN —white ppt. Confirmatory tests in a portion of the urine according to p. 71 under "Albumen."	2. BLOOD —brown or red ppt. Confirmatory tests in a portion of the urine according to p. 72 under "Blood."	3. BILIARY MATTER —greenish ppt. Confirmatory tests in a portion of the urine according to p. 72 under "Bile."

* It must be remembered, however, that the reaction of normal urine is almost always faintly acid.

† If its reaction is neutral or alkaline it must first be rendered faintly acid with acetic acid. ‡ A precipitate soluble in nitric acid merely indicates earthy phosphates.

The following substances are tested for in separate portions of the urine :—

SUGAR—according to p. 72 under “Sugar.” (If albumen has been proved to be present, it must first be removed by boiling the urine which has been faintly acidulated. The latter is then filtered and tested for sugar.)

INDICAN.—A portion of the urine is mixed with its own volume of concentrated hydrochloric acid, two or three cubic centimetres of chloroform, and then a strong solution of bleaching powder is added drop by drop, vigorously shaking after each addition of the latter. If indican is present, the chloroform acquires a blue colour. (Excess of bleaching powder destroys the colour). Albumen, if present, must be removed from the urine by boiling before applying this test.

SULPHURETTED HYDROGEN—is recognised by the odour of the urine, and by the blackening produced when a drop of the excretion is placed on blotting paper soaked in acetate of lead.

AMMONIA—is detected by mixing 100 c.c. of the urine with excess of milk of lime in a flask, and hanging in its neck a piece of turmeric paper, which becomes brown if ammonia salts are present.

PHENOL.—One litre of the urine is distilled with 30 c.c. of concentrated sulphuric acid. The distillate gives the characteristic reaction with bromine water, p. 91. (under “Phenol,” test 1.)

ACETONE.—Urine occasionally contains substances—the exact nature of which is unknown—which give acetone on distillation. Such urine generally has a fruity smell, and gives a claret-red coloration with ferric chloride. To detect the acetone with certainty very large quantities of the urine are fractionally distilled (50 litres or more) with tartaric acid, and the acetone separated from the distillate.

ALCOHOL—may be separated from large quantities of urine by fractional distillation.

TABLE XIV.

Examination of Urinary Sediments.

The reaction is first ascertained. The urine is then placed in a tall conical glass, and when the sediment has settled the clear liquid is decanted as far as possible. Portions of the remaining sediment are then removed with a pipette, and examined as follows :—

MICROSCOPIC EXAMINATION.

A droplet of the sediment is placed on a slide, a cover glass is then placed on it, and a microscopic examination made with a power magnifying 200 diameters, or if the deposit is organized, with one magnifying 400 diameters. The deposit may be :—

CRYSTALLINE.	AMORPHOUS.	ORGANIZED.
<ol style="list-style-type: none"> 1. Lozenge-shaped crystals and other forms (usually yellow)—URIC ACID. 2. Stellate crystals or three-sided prisms—PHOSPHATE OF AMMONIUM AND MAGNESIUM.* 3. Octohedra or dumb bell-shaped crystals—OXALATE OF LIME. 4. † Rosette-like tables—CYSTINE. 	<ol style="list-style-type: none"> 1. Soluble when warmed—URATES. 2. (A) Soluble in acetic acid (a drop being placed at the side of the cover glass, and a piece of filter paper at the opposite side)—PHOSPHATE OF LIME. (B) Soluble in acetic acid, with production of gas bubbles—CARBONATE OF LIME. 3. Rounded globules, with dark edges, soluble in ether—FAT. 	<ol style="list-style-type: none"> 1. Granulated corpuscles in stringy aggregations—MUCUS. 2. Irregularly-shaped scales or cells—EPITHELIUM. 3. Detached granulated corpuscles—PUS. 4. Blood corpuscles—BLOOD. 5. Spermatozoa—SEMEN. 6. MICRO-ORGANISMS. 7. Cylindrical bodies—TUBE CASTS.

CHEMICAL EXAMINATION.

Ascertain the reaction of the sediment with litmus paper, and heat in a test tube with water.

IT DISSOLVES.	IT IS INSOLUBLE, BUT DISSOLVES IN ACETIC ACID.	INSOLUBLE IN ACETIC, BUT SOLUBLE IN HYDROCHLORIC ACID.	INSOLUBLE IN HCl.
Probably— URATES . Confirm by the murexide test, p. 71 under "Urates."	Probably PHOSPHATE OF LIME or PHOSPHATE OF AMMONIA and MAGNESIA , or CARBONATE OF LIME (in the latter case it dissolves with effervescence).	Reprecipitated on adding excess of ammonia— CALCIUM OXALATE .	Probably— URIC ACID . see p. 71, under "Urates."

* If the sediment consists of this substance, the urine almost invariably contains free ammonia.

† From diabetic urine—uric acid is often deposited in large rosettes.

TABLE XV. Examination of Calculi containing One Constituent.

If large enough the calculus may be sawn through, and its appearance noted, as it often happens that is contains different constituents which have been deposited in layers, each layer having a characteristic appearance.

NAME.	PROPERTIES.	IDENTIFICATION.
URATE CALCULI	Generally reddish-brown in colour. Their surface is not very rough, and they are so hard that a cut surface can be polished.	(1) A fragment burns when heated, leaving only a white ash. (2) When powdered, it dissolves on warming with caustic potash—(evolution of NH_3 indicates urate of ammonium). (3) It gives the murexide reaction, p. 71.
PHOSPHATE CALCULI	Generally white, and crumble easily.	(1) Incombustible when heated, but a fragment is :— (a) Fusible when heated on platinum foil before the blowpipe, if it consists of phosphate of ammonium and magnesium. (b) Infusible before the blowpipe, if it consists of phosphate of calcium. (3) The powdered calculus dissolves in hydrochloric acid, and the solution can be tested in the ordinary way for lime, magnesia, and phosphoric acid.
OXALATE CALCULI	As a rule very small, smooth, and grey: when large, <i>very</i> rough, and dark brown. From their appearance they are often called mulberry calculi. They are hard, and have a crystalline fracture.	(1) A fragment when heated does not burn, but dissolves afterwards in hydrochloric acid with effervescence, and the solution gives no precipitate with ammonia. (2) The powdered calculus dissolves <i>without</i> effervescence in hydrochloric acid, and the solution gives a white precipitate with ammonia.
CYSTINE CALCULI	Yellowish in colour, have a smooth surface, are crystalline, and not very hard.	(1) A fragment burns when heated, and leaves but little ash. (2) The powdered calculus dissolves in ammonia, and the solution gives characteristic crystals on spontaneous evaporation.
XANTHINE CALCULI	Generally cinnamon-brown in colour, and tolerably hard. They acquire a waxy lustre on rubbing, and the layers of which they are composed are easily detachable.	Xanthine may be extracted from the powdered calculus by dilute ammonia. The solution is filtered and evaporated to dryness. The residue (well washed with water) gives characteristic crystalline compounds (1) when heated with nitric acid and nitrate of silver, and (2) when treated with hydrochloric acid.

TABLE XVI.
Examination of Calculi containing Several Constituents.

A fragment of the stone is reduced to a fine powder in a mortar, and the powder is heated in a test tube with dilute hydrochloric acid. Effervescence indicates— CARBONATE OF LIME . The solution is then diluted, boiled for some time, and filtered :—		
Residue (may contain uric acid, xanthine, and calcium sulphate).	Solution (may contain cystine, oxalate of lime, and phosphates, also alkalies, and traces of xanthine and uric acid).	
Digest with ammonia, and filter :—	A portion of the solution is tested for AMMONIA by adding an excess of KHO, warming, and ascertaining whether the escaping vapours have the smell of ammonia, and power of colouring turmeric paper brown, and giving white fumes with hydrochloric acid. The remainder of the solution is mixed with an excess of ammonia, then with an excess of acetic acid.	
Residue (may contain uric acid, and calcium sulphate).	Solution (may contain xanthine).	Solution (may contain phosphate of lime and magnesia).
Wash with water, and test portions of the solution with barium chloride and ammonium oxalate for—	Evaporate to dryness when a yellow residue is left, which when moistened with KHO becomes yellow, then red, and on warming, purple, indicating—	
CALCIUM SULPHATE.		
A residue insoluble in water, and in hydrochloric acid, indicates		
URIC ACID.		
Confirm by the murexide test, p. 71.	XANTHINE.	
	OXALATE OF LIME.	
	CYSTINE.	
		MAGNESIUM PHOSPHATE.
		If no precipitate forms, test for phosphoric acid, with molybdate of ammonium.

TABLE XVII.

Examination of Complex Organic Mixtures, such as Articles of Food, the Contents of the Stomach, etc., for Poisons.

Investigations of this kind in actual cases of poisoning, or of suspected poisoning, should be performed only by a specialist, as a high amount of skill and experience are usually required, and the issues at stake are generally very serious: but the student ought to be acquainted with the *methods* which are employed, and should be able to use them for himself in artificial mixtures for practice, or where animals have been poisoned, etc.

One or other of two cases may occur in actual practice. First, from the symptoms (if the poison has been administered), or from the odour or appearance of the suspected mixture, indications of the nature of the poisonous material are furnished. Secondly, there may be no such indications whatever; in which case of course the investigation is usually much more difficult and tedious. The general plan which is then adopted is as follows:—

1. Volatile poisons such as phosphorus, hydrocyanic acid, alcohol, chloroform, carbolic acid, etc., are sought for by distilling the suspected mixture, (which must of course be fluid or semi-fluid)
2. An attempt is made to extract alkaloids from the residue of the first operation
3. The residue from this (second) process is submitted to an investigation to detect poisonous metallic salts, and mineral acids.

PRELIMINARY EXAMINATION.

1. Notice the odour, if any, and draw what conclusions you can.
2. Examine the reaction and appearance of the suspected matter, and see whether it is luminous in the dark (phosphorus).*
3. If there is reason to suspect arsenic, stir some of the substance in a roomy beaker with distilled water persistently, and examine the bottom of the beaker from time to time for hard grains of arsenious anhydride.

SYSTEMATIC EXAMINATION.

1. **Investigation for volatile poisons**:—Reserve from one-third to two-thirds (according to circumstances) of the suspected mixture, and proceed with the rest as follows:—

Make a preliminary investigation for **PHOSPHORUS** by placing the suspected mixture in a flask, and hanging in the neck from a cork, two strips of paper, one moistened with nitrate of silver solution, the other with acetate of lead (best in alkaline solution). Gently warm the flask in the dark and observe whether one or both of the papers are darkened. If the silver paper alone is blackened phosphorus is present, but if both papers are changed, the blackening may be due to sulphuretted hydrogen only.

* If ammonia is present the luminosity may be prevented, but acidulation with tartaric acid will cause it to appear.

TABLE XVI.—Continued.

A preliminary test for **HYDROCYANIC ACID** may also be made by suspending a strip of paper in the neck of the flask, moistened with tincture of guaiacum and sulphate of copper.* Tartaric acid should be added to the suspected mixture until it shows an acid reaction, and it must be warmed to 40–50°C. Should the paper *not* become blue, the *absence* of hydrocyanic acid may be considered as proved: but the fact that it becomes blue is no positive proof of the presence of the acid, as many substances in addition to it, produce that effect. Whether these preliminary experiments have given an indication of the two poisons (*i.e.* phosphorus or hydrocyanic acid) or not, the suspected mixture (acidulated with tartaric acid) is next heated† in a distilling flask connected with a Liebig's condenser *in the dark*, when if free phosphorus is present, a luminous ring is seen at that spot in the inner tube of the condenser where the distilling vapour begins to condense, and eventually small yellow globules of phosphorus collect in the receiver.‡ Should no phosphorus be found, the watery distillate must be examined for hydrocyanic acid and other volatile poisons.

The first portions of the distillate (which should be collected separately) are tested as follows, after carefully noticing the odour:—

1. A small quantity is mixed with a drop or two of pure caustic potash or soda solution, then a few drops of ferrous sulphate solution are added, and the mixture well shaken until it darkens in colour. Hydrochloric acid is then added very cautiously to acid reaction, when, if hydrocyanic acid is present, a blue precipitate or greenish-blue solution is produced.
2. Another quantity is mixed with a few drops of pure caustic potash or soda solution, then a few drops of yellow sulphide of ammonium are added, and the mixture evaporated to dryness on a water bath. The residue is then treated with a drop or two of dilute hydrochloric acid (so that it has an acid reaction), and after a few minutes ferric chloride is added, which will produce a blood-red coloration if hydrocyanic acid is present.

As regards the other volatile poisons, such as chloroform, carbolic acid, etc., the smell and other characteristic properties of the distillate (and probably of the original substance also) generally afford a pretty sure indication of their presence. In such cases special tests must be applied to the distillate, see pp. 86, 87, and 91.

2. Investigation for alkaloids:—The suspected matter should be fairly free from water.|| It is mixed with double its weight of alcohol as free as possible from fusel oil,§ and from 15 to 30 grains of pure tartaric acid dissolved in alcohol, and the mixture digested in a flask at a gentle heat (70–75°C). On cooling, it is thrown on to a filter, then washed with pure alcohol. The alcoholic extract contains the whole of the alkaloids.

* The reaction which occurs is based upon the separation of active oxygen which strikes a blue colour with the resin of guaiacum. Thus:— $3\text{CuSO}_4 + 4\text{HCN} + \text{H}_2\text{O} \equiv \text{Cu}_2(\text{CN})_2 + \text{Cu}(\text{CN})_2 + 3\text{H}_2\text{SO}_4 + \text{O}$.

† It may be necessary to dilute it with water before distilling.

‡ The water in the receiver contains phosphorous acid—if phosphorus is present. It should be mixed with strong chlorine water to convert it into phosphoric acid, then evaporated to a small bulk, and tested with (1) molybdate of ammonium, and (2) magnesia mixture.

|| If previously diluted it must be first evaporated on a water bath—taking care that during the evaporation its reaction is *faintly* acid with tartaric acid. If much of the latter has been previously added, the mixture must be nearly neutralized with carbonate of soda.

§ The purest absolute alcohol of commerce should for this purpose be rectified twice from a little tartaric acid, in order to free it from the bases which are present in fusel oil.

It is evaporated over a water bath at a low temperature (the temperature of the water in the bath may be kept at 80°C, by which means the temperature of the evaporating mixture does not rise above 40–50°C), or where great caution is necessary it may be evaporated in vacuo over sulphuric acid at ordinary temperatures. If, as usually happens, fat, etc., separate out, the mixture is filtered through paper previously moistened with distilled water, and the residue carefully washed. The filtrate is evaporated in vacuo over sulphuric acid, the solid residue completely exhausted by cold alcohol, and the extract evaporated in vacuo. The new residue is dissolved in the smallest possible quantity of cold distilled water, and the solution at once introduced into a long narrow flask which will hold about five times the bulk of the fluid. Bicarbonate of potash is then added until effervescence ceases, then the flask is nearly filled with ether, the mixture thoroughly shaken for several minutes, and allowed to rest. A drop or two of the clear ethereal extract is then placed on a watch glass, and allowed to evaporate spontaneously in a dry place.

A. Should a *liquid alkaloid* be indicated by the nature of the residue (oily drops with pungent odour on warming), solution of caustic potash is added to the contents of the flask, which are again well shaken, the ether decanted off, and the residue exhausted by three or four more additions of ether. All the ethereal extracts are united in a larger flask, and to them are immediately added two cubic centimeters of water acidulated with a fifth of its weight of pure sulphuric acid. The flask is shaken for some time, and then allowed to rest. The ether is next decanted, and the acid liquid washed with a new quantity of ether. The alkaloid is now in the form of a sulphate, and remains dissolved in the acidulated water. In order to extract it, excess of caustic potash or soda solution is added, and the mixture is exhausted by several successive additions of pure ether. The ethereal solution is allowed to evaporate spontaneously, when it leaves the alkaloid in a state of great purity.

B. Should a *solid alkaloid* be indicated, the contents of the flask are treated as before with caustic soda solution and ether, and the ethereal solution evaporated. A little dilute sulphuric acid is next added, the solution filtered, and the residue washed with water. Both filtrate and washings are then concentrated in vacuo to $\frac{3}{4}$ of their bulk, then mixed with excess of carbonate of potash, and the mixture exhausted with absolute alcohol, which on evaporation leaves the alkaloid in a pure state.

In either case the alkaloid is identified by the tests given in Table XI. or XII.

3. Investigation for poisonous metallic salts :—A portion of the suspected matter is acidulated strongly with hydrochloric acid, and a few crystals of potassium chlorate added, the mixture is then warmed on the water bath until it becomes entirely decolorized. Water is next added, and the liquid boiled until it ceases to smell of chlorine. Filter, and examine filtrate for metals by Table VIII.*

4. Investigation for poisonous mineral acids :—The presence of these acids is indicated by the highly inflamed appearance of the viscera, by the strong acid reaction of the suspected matter, and its effervescence with sodium carbonate. When this is the case a portion of the suspected matter is boiled with water, filtered, and the filtrate examined for the acids by Table IX.

* When examining for metals of Sub-grs. 2 and 3 of Gr. 1, care should be taken that the sulphuretted hydrogen gas is passed through the solution for several hours.

Properties and Reactions of certain other Organic Bodies.

FORMIC ACID— H_2CO_2 .

When pure, formic acid is a slightly fuming liquid, having a pungent and characteristic odour. It boils at 99°C , and is miscible in all proportions with water, alcohol, and ether. Its salts are as a rule readily soluble—formiate of lead being the least so. Both the free acid and its salts are powerful reducing agents.

1. Formic acid and its salts (in the solid state) are decomposed when heated with strong sulphuric acid, carbonic oxide being formed. Thus :— $\text{CH}_2\text{O}_2 - \text{H}_2\text{O} = \text{CO}$.
2. On warming a solution of a formiate with dilute sulphuric acid, formic acid is liberated and may be recognized by its odour ; also by suspending a piece of paper moistened with nitrate of silver in the fumes, which becomes blackened owing to the reduction of the silver.
3. On warming a formiate with alcohol and strong sulphuric acid, formic ether is produced $\text{CHO}_2(\text{C}_2\text{H}_5)$, which has a characteristic odour resembling rum.
4. Solutions of formiates when warmed with nitrate of silver give a black precipitate of metallic silver.
5. Solutions of formiates when warmed with mercuric chloride give either a white precipitate of calomel, or a grey precipitate of metallic mercury.
6. Formiates behave with ferric chloride, like acetates.

BUTYRIC ACIDS— $\text{C}_4\text{H}_8\text{O}_2$.

The *normal* acid $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COOH}$ is a colourless oily liquid having a powerful and characteristic odour. It boils at 163°C . The *iso* acid $(\text{CH}_3)_2 = \text{CH} - \text{COOH}$ much resembles the normal body, but boils at 154°C . Both are only sparingly soluble in water.

1. On warming a butyrate with sulphuric acid, butyric acid is set free, and is easily recognized by its odour.
2. On warming a butyrate with alcohol and strong sulphuric acid, butyric ether $\text{C}_4\text{H}_7\text{O}_2(\text{C}_2\text{H}_5)$ is produced, having a very characteristic odour like pine apples.
3. Acetate of lead gives a white precipitate with solutions of butyrates $(\text{C}_4\text{H}_7\text{O}_2)_2\text{Pb}$, which on warming melts to an oil.
4. Nitrate of silver gives a white, cheesy or crystalline precipitate $\text{C}_4\text{H}_7\text{O}_2\text{Ag}$.
5. Ferric chloride gives a brownish-yellow precipitate.

LACTIC ACIDS— $C_3H_5O_3$.

Three isomers are known (1) ordinary or fermentation lactic acid (α -oxypropionic acid), or ethylidene lactic acid, $CH_3-CH(OH)-COOH$, *optically active*; (2) sarko-lactic acid, which only differs in being *inactive*; (3) ethylene lactic acid, (β -oxypropionic acid), $CH_2(OH)-CH_2-COOH$. All three are syrupy liquids having no odour. They are soluble in all proportions in water and alcohol, and dissolve readily in ether also. Heated to $130-150^\circ C$. the first two lose water, and give suffocating vapours of the anhydrides. The reactions of ordinary lactic acid are as follows:—

1. Heated with *dilute* sulphuric acid, lactic acid, and lactates, yield acetaldehyde and formic acid.
2. Heated with strong sulphuric acid, carbonic oxide is evolved.
3. The most characteristic salts are the calcium salt, crystallizing in tufts of needles, and soluble in about 10 parts of cold water; the zinc salt, crystallizing in needles and club-shaped crystals, soluble in about 60 parts of cold water; the magnesium salt, crystallizing much like the zinc salt, and soluble in about 30 parts of cold water.

SUCCINIC ACIDS— $C_4H_6O_4$.

Of these, ethylene succinic acid $HOOC-CH_2-CH_2-COOH$ is alone of importance. It is solid, and crystallizes in colourless monoclinic prisms. It is soluble in about 23 parts of water at ordinary temperatures, and in about 4 parts of boiling water. When heated, it partly sublimes, and partly loses water to give the anhydride.

1. On cautiously warming a solid succinate with about twice as much bisulphate of potash, free succinic acid is formed, and condenses in the cold part of the tube, partly in crystals, partly in the form of oily drops which solidify on cooling.
2. Chloride of barium precipitates moderately strong solutions of succinates when the mixture is stirred. The separated crystals have a very characteristic appearance when examined under the microscope. With dilute solutions of succinates, 1—2 volumes of alcohol must be added in order to obtain the barium salt.
3. Ferric chloride gives a pale rust coloured gelatinous precipitate of basic ferric succinate.
4. Acetate of lead gives a white amorphous precipitate which redissolves both in excess of the succinate and in acetate of lead. On standing, however, the salt soon separates in the crystalline state.

MALIC ACID— $C_4H_6O_5$.

The acid is a solid crystalline substance, and dissolves readily in water and in alcohol. When heated, it is resolved into water, maleic acid, and fumaric acid, the two last forming a crystalline sublimate in the upper part of the tube.

1. Malic acid and its salts when heated with sulphuric acid evolve carbonic oxide and carbonic anhydride. The fluid then darkens, and ultimately becomes black.
2. Chloride of calcium gives no precipitate with malic acid or malates, even when the mixture is boiled (unless the solution is very strong). On adding 2 volumes of alcohol, a voluminous white precipitate of malate of calcium is thrown down $(C_4H_4O_5)Ca, 3H_2O$.

3. Acetate of lead throws down a white precipitate $C_4H_4O_5Pb$, $3H_2O$, which fuses when heated to a resinous mass.
4. Nitrate of silver gives a white precipitate $C_4H_4O_5Ag_2$, which on long standing, or on warming, turns somewhat grey.

BENZOIC ACID— $C_7H_6O_2$.

Benzoic acid forms white feathery crystals, which melt at $121.4^\circ C$, and volatilize slowly even at lower temperatures. The vapour of benzoic acid has a very characteristic aromatic odour. The acid is very sparingly soluble in cold water, more readily in hot water, and dissolves easily in alcohol, ether, alkalies, and to some extent in solution of phosphate of soda. Most benzoates are soluble in water.

1. Solid benzoic acid and benzoates when distilled with lime evolve benzol :—

$$C_6H_5-COOH + CaO = C_6H_6 + CaCO_3.$$
2. Solutions of benzoates, unless very dilute, give a precipitate of benzoic acid with sulphuric acid (or other mineral acid), and on warming the mixture, the characteristic odour of benzoic acid is evolved.
3. Solutions of benzoates when heated with alcohol and strong sulphuric acid emit the characteristic odour of benzoic ether ($C_7H_5O_2$) C_2H_5 .
4. Solutions of benzoates give (in neutral solutions) a buff coloured precipitate of basic ferric benzoate $Fe_2(C_7H_5O_2)_6$, Fe_2O_3 .
5. Solutions of benzoates give a white flocculent precipitate $(C_7H_5O_2)_2Pb$, H_2O , soluble in excess of acetate of lead and in acetic acid.

Carbohydrates.

Form an important group of organic compounds—chiefly of vegetable origin. In addition to carbon they all contain hydrogen and oxygen in the proportions necessary to form water—whence their name. All carbohydrates contain either six atoms of carbon or a multiple of six.

As a class they possess the following characteristic properties, either before or after hydrolysis :—

1. They reduce easily reducible metals from their solutions.
2. They give a yellow colour with alkalies.
3. Heated with sulphuric or hydrochloric acid they decompose giving lævulinic acid, humus-like substances, and formic acid.
4. They give with acetate of phenyl hydrazine, after a short time, a precipitate which usually consists of yellow needles.
5. Nearly (and perhaps) all carbohydrates rotate the plane of a ray of polarized light.

GLUCOSES— $C_6H_{12}O_6$.

Dextrose (grape sugar)—soluble in water and in alcohol. It rotates the ray of polarized light to the *right*.

1. Reduces *Fehling's solution** at once when the mixture is warmed, red Cu_2O being precipitated.

* *Fehling's solution*—prepared by mixing equal volumes of the following solutions just prior to use :—

1. 34.64 grams. of pure sulphate of copper dissolved in water, so that the mixture occupies (just) 500 cc.
2. 173 grams of Rochelle salt and 60 grams of caustic soda dissolved in water, so that the mixture occupies 500 cc.

2. Concentrated sulphuric acid does not blacken solid dextrose.
3. Heated with strong caustic potash solution the mixture turns brown.
4. Readily ferments with yeast.
5. Allowed to stand at ordinary temperatures with normal acetate of copper, or warmed with a mixture of that salt and acetic acid, and then allowed to stand, reduction and precipitation of cuprous oxide occurs.

Lævulose resembles dextrose in most of its properties, but rotates the ray of polarized light to the *left*.

SACCHAROSES— $C_{12}H_{22}O_{11}$.

Cane Sugar or sucrose—crystallizes in colourless monoclinic prisms (sugar candy), and has a very sweet taste. Easily soluble in water, and sparingly soluble in alcohol. Heated it melts, and on cooling solidifies to a glassy mass (barley sugar). Heated more strongly it turns brown, and decomposes, evolving vapours of characteristic odour. It rotates the ray of polarized light to the *right*.

1. When warmed with *Fehling's solution* no change occurs at first, but on prolonged boiling, very slow reduction occurs.
2. Concentrated sulphuric acid blackens solid cane sugar and its strong aqueous solution.
3. Heated with strong caustic potash solution the mixture does not turn brown.
4. Allowed to stand at ordinary temperatures with normal acetate of copper solution, or warmed with a mixture of that salt and acetic acid and then allowed to stand, no reduction occurs.

Milk Sugar or lactose— $C_{12}H_{22}O_{11}$, H_2O forms hard prisms which are not so sweet as cane sugar. It is less soluble in water. Like cane sugar it is dextro-rotatory.

1. Readily reduces *Fehling's solution* on warming, cuprous oxide being precipitated.
2. Concentrated sulphuric acid chars it, but less readily than cane sugar.
3. Heated with strong caustic potash solution, the mixture turns brown.
4. Allowed to stand at ordinary temperatures with normal acetate of copper solution, no reduction occurs. If a little acetic acid is added, the mixture boiled for a short time, and then allowed to stand, there is also no reduction if the solution is not too concentrated.

AMYLOIDS— $(C_6H_{10}O_5)_n$.

Starch—forms a white amorphous powder. When examined with the microscope it shows a characteristic structure, each granule showing concentric laminæ, and resembling to a certain extent an oyster shell. The size of the granules varies considerably with the different varieties of starch. When starch is rubbed into a thin paste with cold water, the granules burst and discharge their contents, forming a thick translucent gelatinous mass—or if very little of the starch is present a translucent fluid.

1. Boiled starch paste is precipitated by alcohol; also by basic acetate of lead, baryta water, lime water, tannin, &c.
2. Starch, especially after it has been boiled with water, gives a deep blue colour, with free iodine. The colour is destroyed by heat. This is the most delicate and characteristic test for starch.

3. Starch when boiled with dilute mineral acids, gives a mixture of dextrin and dextrose, or when treated with diastase, and certain other unorganized ferments—dextrin and maltose. The formation of dextrose occurs according to the equation— $(C_6H_{10}O_5)_n + nH_2O = n(C_6H_{12}O_6)$.
4. When heated to $150^{\circ}C$, starch is converted into dextrin which readily dissolves in water, and gives no blue colour with iodine.

Dextrin—an amorphous powder, readily soluble in water, forming a mucilaginous solution. It has no sweet taste. There are probably several varieties.

1. Dextrin (obtained by heating starch) gives a wine-red colour with free iodine.
2. Allowed to stand at ordinary temperatures with normal acetate of copper, no reduction occurs, but on warming, gradual reduction takes place. If a little acetic acid is added to the mixture and it is boiled for a short time, and then allowed to stand, no change takes place.
3. When boiled with dilute mineral acids, dextrin is converted into dextrose. Thus :—
$$(C_6H_{10}O_5)_n + nH_2O = n(C_6H_{12}O_6)$$
4. *Fehling's solution* behaves with dextrin as with dextrose, but reduction does not occur quite so rapidly.

Cellulose—Solid substance, retaining the structure of the plant fibre from which it has been obtained (*e.g.*, cotton wool). Insoluble in all liquids, except strong sulphuric acid (which dissolves it in the cold, and cupric hydrate dissolved in ammonia).

1. When dissolved in strong sulphuric acid, and the mixture diluted and boiled, cellulose is converted into dextrose. Thus :— $(C_6H_{10}O_5)_n + nH_2O = n(C_6H_{12}O_6)$.

Gum (arabic)—consists of compounds of arabic acid— $(C_6H_{10}O_5)$ at $120^{\circ}C$, $C_{12}H_{22}O_{11}$ at $100^{\circ}C$ —with lime and potash. It forms white or slightly yellow transparent or translucent masses. It is soluble with ease in water, forming a mucilaginous liquid, and this solution (if fairly strong) gives a white precipitate with strong alcohol of the original substance. But if hydrochloric acid is previously added, the precipitate consists of arabic acid. Iodine gives no colour with gum, thus distinguishing it from dextrin.

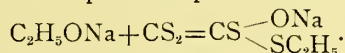
1. On adding to a gum solution a few drops of sulphate of copper, and then excess of caustic soda, a bluish precipitate is produced, which when boiled is not reduced nor blackened. (This reaction distinguishes gum from dextrin and the sugars.)
2. Basic acetate of lead gives a white gelatinous precipitate—a reaction which distinguishes gum from dextrin, the sugars, and gelatine.

ALCOHOL— C_2H_6O

Is a colourless liquid, lighter than water. Has a burning taste and characteristic odour. It boils at $78.4^{\circ}C$, and burns when ignited with a blue flame. It is miscible with water and with ether in all proportions, and when pure, with bisulphide of carbon also.

1. When warmed with bichromate of potash and sulphuric acid, the characteristic odour of aldehyde C_2H_4O is emitted, and the solution turns green.
2. When warmed with a solution of iodine in iodide of potassium, and then just enough caustic soda solution added to decolorize the mixture, iodoform CHI_3 is produced as a yellow crystalline precipitate. This has a very characteristic appearance when examined with the microscope, the crystals consisting of hexagonal plates or six rayed stars. The crystals and the fluid from which they separate have also a very characteristic saffron-like odour. This reaction is not absolutely characteristic of alcohol, as aldehyde, acetone, acetic ether, and some other substances, also yield iodoform.

3. If strong alcohol is mixed with a solid alkaline, acetate, benzoate, or formiate, and strong sulphuric acid, the mixture when warmed evolves the characteristic odours of the respective ethers.
4. If bisulphide of carbon is mixed with a solution of caustic potash in pretty strong alcohol, a yellow solution of xanthate of potash is produced—



On adding sulphate of copper, and slightly acidulating with hydrochloric acid, a yellow precipitate of xanthate of copper is produced.

[Tests 3 and 4 succeed only with strong alcohol. This can be separated from a weak solution by distillation—the first portions which pass over being rectified two or three times, if necessary, from solid carbonate of potash.]

CHLOROFORM— CHCl_3

Is a colourless mobile liquid which is not combustible. It has a characteristic odour and a burning taste. It boils at 61.2°C , and dissolves in alcohol and ether in all proportions, but is almost insoluble in water.

1. On warming chloroform with a strong aqueous solution of caustic potash or soda, to which about ten times as much alcohol has been added, it is rapidly decomposed, giving a mixture of chloride and formiate of the alkali— $\text{CHCl}_3 + 4\text{KHO} = 3\text{KCl} + \text{CHKO}_2 + 2\text{H}_2\text{O}$. The formic acid may be separated by boiling off the spirit, and distilling the residue with dilute sulphuric acid.
2. On warming a drop or two of chloroform with a mixture of alcoholic potash, and a drop or two of aniline, the intense and disagreeable, but characteristic odour of phenyl iso-nitrile is evolved— $\text{CHCl}_3 + \text{NH}_2(\text{C}_6\text{H}_5) + 3\text{KHO} = \text{CN}(\text{C}_6\text{H}_5) + 3\text{KCl} + 3\text{H}_2\text{O}$.

The purity of chloroform is known by the following properties :—

1. When evaporated on the hand or in a watch glass it should leave no residue and no odour.
2. When shaken with nitrate of silver solution it should not cause any turbidity.
3. It should not redden litmus.
4. It should not colour a mixture of bichromate of potash and sulphuric acid green in the cold.
5. When boiled with bright metallic sodium the lustre of the metal should not be dimmed.
6. It should not be coloured brown by caustic potash, nor by strong sulphuric acid.

CHLORAL HYDRATE— $\text{C}_2\text{H}_3\text{Cl}_3\text{O}_2$

Is a solid crystalline body, which when rubbed in the hand has a fatty feel. It has a strong and characteristic odour and a nauseous bitter taste. When heated it melts, then boils, and its vapour condenses in oily drops, which crystallize on cooling. It dissolves easily in water, alcohol, and ether. When thrown on to water, the particles of chloral hydrate gyrate and move about the surface.

1. On adding caustic potash or soda to a fairly strong solution of chloral hydrate, the fluid becomes milky from the separation of chloroform, the odour of which becomes apparent on warming—



2. On adding nitrate of silver to a cold solution of chloral hydrate very little if any effect is produced, but on adding a little ammonia the odour of chloroform becomes apparent, and the silver is reduced partly in the form of a mirror.
3. Chloral hydrate when warmed with aniline and alcoholic caustic potash gives the characteristic odour of phenyl iso-nitrile.

GLYCERINE— $C_3H_8O_3$

When pure, is a colourless syrupy liquid, having a sweet taste. It attracts moisture from the air, and is miscible in all proportions with water and alcohol. It is almost insoluble in ether, but dissolves abundantly in a mixture of alcohol and ether.

1. On moistening a piece of paper with a drop of glycerine the paper becomes marked as with a grease spot, but on washing the paper with water and then drying, the spot is removed.
2. On heating glycerine in a test tube with bisulphate of potash or phosphoric acid, suffocating vapours of very characteristic odour are produced. They consist of acroleine— C_3H_4O .

[If a solution has to be tested for glycerine it must first be concentrated as far as possible on a water bath.]

ALBUMENOID BODIES.

These form the chief part of the organic constituents of animals, and some occur in vegetables also. They contain carbon, hydrogen, nitrogen, oxygen, and sulphur, and there can be no doubt have an exceedingly complex composition. They are usually amorphous, and their solutions are levorotatory. With the exception of peptones they do not diffuse. They may be divided into the following groups :—

Albumens (*serum, egg, plant albumen, &c.*)—Soluble in water, and coagulated by heat.

Peptones—Soluble in water, and not coagulated by heat. (Peptones are formed by the action of gastric juice, pancreatic ferment, etc., or of boiling dilute acids and alkalies on albumenoid bodies.)

Globulines (*myosine, globuline, fibrinogen, &c.*)—Insoluble in water, but soluble in dilute salt solution.

Derived Albumens (Albumenates) (*acid albumen, alkali albumen, caseine, &c.*)—Insoluble in water and in salt solution. Soluble in dilute acids and alkalies.

Fibrins—Insoluble in water, sparingly soluble in dilute acids, alkalies, and in neutral saline solutions.

The following reactions are general for all albumenoid bodies :—

1. When heated they char, and evolve vapours having the odour of singed hair, and containing abundance of ammonia. The vapours condense in part on a cold surface, and give reddish oily drops.

2. When boiled with strong alkalies, ammonia is disengaged and the residual solution contains an alkaline sulphide. Hence it evolves sulphuretted hydrogen when treated with an excess of acid, and gives a violet colour with nitro-prusside of sodium.
3. Strong acetic acid dissolves nearly all albumenoids when warmed with them, and from the solutions thus obtained ferrocyanide of potassium throws down a white precipitate.
4. Fairly strong hydrochloric acid when heated with albumenoid bodies decomposes them, the fluid becoming violet, and finally brown.
5. Strong nitric acid colours albumenoids yellow, and on moistening the stain with alkalies, the colour becoming brownish-yellow. (Xantho-proteine reaction.)
6. When an albumenoid body is mixed with a cold solution containing 2—3 volumes of strong sulphuric acid to 1 volume of water and a few drops of a strong solution of cane sugar, a red colour gradually appears—(in about half-an-hour), and in 24 hours the mixture is nearly black.
7. When warmed with *Millon's reagent*,* albumenoid bodies acquire at first a yellow, then a red colour.
8. On adding a drop of sulphate of copper solution to an albumenoid dissolved in caustic soda, and shaking the mixture, the hydrate of copper redissolves and colours the fluid violet. The colour does not disappear on boiling.

BLOOD.

1. Blood when examined under the microscope presents a very characteristic appearance. Numerous discs or *corpuscles* are then seen to be floating in a colourless liquid. The size of the corpuscles varies in different animals. Addition of water changes their form, but solutions of certain salts do not do so. A solution of iodide of potassium in four times its weight of water is most suitable for the purpose. Linen, &c., stained with blood may be macerated in this solution, and after remaining three or four hours the corpuscles can be seen in a drop of the liquid squeezed out.
2. Alkalies decompose the hæmoglobin of blood into globulin and hæmatin. If a few drops of caustic potash or soda are added to a mixture of water and blood, the solution exhibits dichroism, being red by reflected, and green by transmitted, light.
3. If dried blood is warmed with glacial acetic acid, and a very little common salt, hæmin (hydrochlorate of hæmatin— $C_{32}H_{30}N_4Fe_2O_3$, HCl) is produced. A drop of the solution when allowed to evaporate spontaneously gives minute, but highly characteristic, crystals (*Teichmann's crystals*), which are brown, or brown-red, by transmitted light, but violet, or bluish-black, by reflected light, with a metallic lustre. Crystals of hæmin are further characterized by being insoluble in water, alcohol, ether, &c., but they dissolve in caustic soda, forming a solution which is greenish in thin layers.

This test is delicate and characteristic, and is frequently employed for recognizing blood spots and stains.

4. A solution of blood, even when very dilute, exhibits two very characteristic absorption bands when examined with the spectroscope.

* Prepared by gently warming mercury with an equal volume of strong nitric acid until it is dissolved, then diluting the liquid with twice its bulk of water, and allowing the fluid to settle. Or by adding to a neutral solution of mercuric nitrate a drop or two of red fuming nitric acid.

5. When blood is added, even in very minute quantity, to a mixture of equal volumes of turpentine and tincture of guaiacum a blue colour is produced almost instantly. (The blue colour is caused by the oxidation of the resin contained in the guaiacum tincture, and is produced even when blood is diluted with 10,000 times its volume of water ; but it is not absolutely characteristic, as many inorganic and organic substances—such as flour, gum, milk, etc., give it also.)

TANNINS

Are abundantly distributed in the vegetable kingdom, and cause the astringency of plants. Their reactions are not quite identical, though similar—the most important is ordinary tannin :—

Digallic Acid (gallotannic acid)— $C_{14}H_{10}O_9$.—which when pure forms a pale yellow powder, having an astringent taste. It dissolves easily in water and in alcohol, and to a less extent in ether, though it is easily soluble in acetic ether. It combines with bases, forming salts, which for the greater part are insoluble. Its alkaline salts are exceptions to this rule. Acids precipitate its aqueous solution.

1. When cautiously warmed, tannin melts and yields (among other bodies) pyrogallic acid, which volatilizes and condenses in yellowish drops, becoming crystalline on cooling.
2. When warmed with strong sulphuric acid to $150^{\circ}C$ tannin is converted into rufigallic acid and other bodies. The mixture is thrown into water, and the turbid liquid thus obtained shaken with acetic ether. The acetic ether is then drawn off, washed by shaking with water, and evaporated to dryness on a water bath. By this means tolerably pure rufigallic acid is obtained. It is characterized by giving a carmine-red solution with cold sulphuric acid, and a transient blue colour with strong caustic potash solution.
3. On adding an excess of caustic soda to a solution of tannin, a reddish-yellow colour is produced, which rapidly changes on contact with air through various shades of red-brown, red, brown-yellow, and yellow. The reaction is delicate.
4. Ferric chloride gives a blue-black precipitate in a solution of tannin, or if the latter is very weak a blue-black colour. (This reaction does not succeed if the tannin solution contains acids or alkalies.)
5. Sulphate of cinchonine precipitates nearly the whole of the tannin from a solution, in the form of a white compound.
6. A freshly prepared solution of gelatine gives with a solution of tannin a white ropy precipitate, which, after washing, is coloured black by ferric chloride, and red by caustic soda.

GALLIC ACID— $C_7H_6O_5$, H_2O

Crystallizes in slender needles. Dissolves with great ease in boiling water, but less readily in cold water. Soluble readily in alcohol, but with difficulty in ether. Acetic ether also dissolves it. When heated, it behaves in much the same manner as tannin.

1. When heated with strong sulphuric acid to $150^{\circ}C$ it is, like tannin, converted into rufigallic acid (see tannin)— $2C_7H_6O_5 = C_{14}H_8O_8 + 2H_2O$.
2. It behaves with ferric chloride like tannin.

3. It differs from tannin in being crystalline ; in not being precipitated from aqueous solutions by acids ; and in giving no precipitate with gelatine or sulphate of cinchonine..

PYROGALLIC ACID (trioxyphenol)— $C_6H_6O_3$

Forms bulky, colourless needles. Soluble in water, alcohol, and ether. Melts when heated, and volatilizes nearly unchanged.

1. Nitric acid when warmed with pyrogalllic acid attacks it energetically, giving off abundance of red fumes, and producing a yellow solution of extraordinary tinctorial power. 1 part of this solution will colour from 2—3 million parts of water yellow.
2. In the absence of air or oxygen alkalies give a colourless solution with pyrogalllic acid, but in their presence the solutions almost instantly become yellow or brown.
3. Lime-water gives a violet colour, which, however, soon becomes red or brown.
4. A solution of ferrous sulphate (free from ferric salts) gives a colourless solution with pyrogalllic acid, but if the mixture is vigorously shaken it becomes blue. If a trace of caustic soda is previously added to the pyrogalllic solution, ferrous sulphate gives a red liquid, which on shaking becomes violet-blue.
5. Nitrate of silver is almost instantly reduced by pyrogalllic acid.

PHENOL (carbolic acid)— C_6H_6O

When pure, forms colourless deliquescent crystals, melting at $41^{\circ}C$, and boiling at $183^{\circ}C$. It has a persistent and characteristic odour. It is sparingly soluble in water, but dissolves easily in alcohol, ether, chloroform, and alkalies. It volatilizes with steam.

1. Bromine-water gives a white or yellowish precipitate of tribromo-phenol $C_6H_3Br_3O$, even in very dilute solutions (1 in 60,000).
2. Ferric chloride gives a violet coloration.
3. When mixed with nitrite of potassium and strong sulphuric acid, it gives a brown colour, changing to green, and finally to blue.
4. When heated with ammonia and a drop or two of bleaching powder solution, a deep blue colour is produced (green in dilute solutions), changed to red by acids.
5. A pine shaving moistened with hydrochloric acid, is turned purple-red by phenol.

SALICYLIC ACID (orthoxybenzoic acid)— $C_7H_6O_3$

Forms a white granular powder or prismatic crystals. Nearly insoluble in cold water. Soluble in hot water, alcohol, ether, and alkalies. It melts at $155^{\circ}C$.

1. Solid salicylic acid and its salts when distilled with lime yield phenol, which may be identified by its odour, &c.
2. Ferric chloride gives a violet colour, even in very dilute solutions. The colour is destroyed by acids or alkalies.
3. Bromine-water reacts as with phenol, but the reaction is far less delicate.

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